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Patentanmeldung Nr. Patent application No. Demande de brevet n°

02405520.4

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Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.:
Demande n°: 02405520.4

Anmeldetag:
Date of filing:
Date de dépôt: 24/06/02

Anmelder:
Applicant(s):
Demandeur(s):
Ciba Specialty Chemicals Holding Inc.
4057 Basel
SWITZERLAND

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:

Cationic alkoxyamines and their use in producing nano particles from natural or synthetic clays

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:

/

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing:
Etats contractants désignés lors du dépôt:

AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR

Bemerkungen:
Remarks:
Remarques:

Cationic Alkoxyamines And Their Use in Producing Nano Particles from Natural or Synthetic Clays

The instant invention relates to cationic alkoxyamines, which are useful as polymerization initiators/regulators in a controlled stable free radical polymerization process to produce intercalated and/or exfoliated nanoparticles from natural or synthetic clays. The invention also relates to improved nanocomposites produced by this process and to the use of these nanocomposite compositions as, for example, coatings, sealants, caulks, adhesives and as plastic additives.

One way of improving polymer properties is by adding a natural or synthetic clay material to polymers to form composite materials. However, incorporating clays into polymers may not provide a desirable improvement in the physical properties, particularly mechanical and optical properties of the polymer may be adversely affected.

Nanonocomposite compositions containing finely dispersed natural or synthetic clay with at least partially intercalated and/or exfoliated layers and mixtures of ethylenically unsaturated monomers and/or polymers therefrom have therefore attracted much interest in the last years. These materials combine the desired effects of dispersed clay by avoiding the negative influence on, for example, the mechanical or optical properties.

Such compositions, methods for making them and their use in polymers and coatings are for example described in WO 02/24759. Polymerization processes are described using montmorillonite clay, acrylate monomers and for example ammonium persulfate as radical initiator. This conventional polymerization process leads to polymers with broad molecular weight distributions and a high polydispersity index (PD).

Y. Sogah et al., J. Am. Chem. Soc. 1999, 121, 1615-1616 describe the synthesis of dispersed nanocomposite compositions by in situ living free radical polymerization of styrene using a silicate-anchored initiator. The nitroxyl compound used is a 2,2,6,6 tetramethylpiperidine alkoxyamine. Although Sogah et al. have shown the principal possibility of preparing nanocomposite compositions by controlled free radical polymerization, they have been limited to styrene, since the known initiators/regulators are not efficient enough to

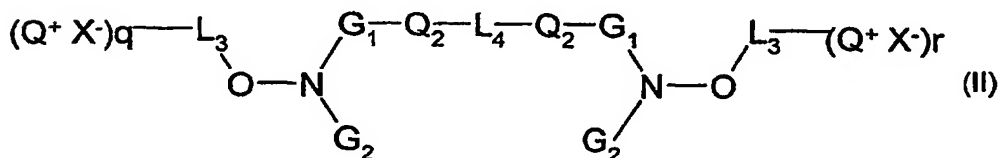
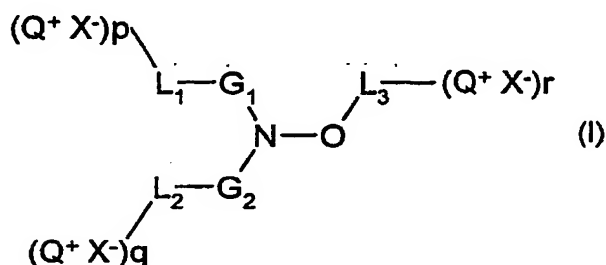
polymerize acrylates or methacrylates with reasonable conversion rates at acceptable temperatures.

The present invention provides alkoxyamines, which can be anchored to natural or synthetic clays by a cationic anchor group and which have a high reactivity towards acrylates, methacrylates, styrene and other monomers resulting in a controlled molecular weight with narrow molecular weight distribution. With these compounds polymerization leads to high monomer to polymer conversions in short times and at relatively low temperatures.

In contrast to conventional radical polymerization, controlled radical polymerization allows to adjust the molecular weight of all growing chains almost uniformly to a predetermined length (low polydispersity), resulting in an almost ideal dispersion of the intercalated and/or exfoliated clay particles.

The nanocomposite compositions of the instant invention can be optically almost transparent, indicating the fine distribution, on the nanometer scale, of the clay.

One aspect of the invention is a compound of formula (I) or (II)



wherein

G₁ and G₂ independently represent a tertiary carbon atom to which unsubstituted C₁-C₁₈alkyl or phenyl or with CN, COC₁-C₁₈alkyl, CO-phenyl, COOC₁-C₁₈alkyl, OC₁-C₁₈alkyl, NO₂, NHC₁-C₁₈alkyl or N(C₁-C₁₈)₂alkyl substituted alkyl or phenyl groups are bonded; or one of

G₁ and G₂ is a secondary carbon atom to which a group -P(O)(OR₂₂)₂ and the other is as defined above; or

G₁ and G₂ together with the nitrogen atom to which they are bonded to form a 5 to 8 membered heterocyclic ring or a polycyclic or spirocyclic 5 to 20 membered heterocyclic ring system, which is substituted with 4 C₁-C₄alkyl groups or 2 C₅-C₁₂ spirocycloalkyl groups in ortho position to the nitrogen atom and which may be further substituted with one or more C₁-C₁₈alkyl, C₁-C₁₈alkoxy or =O groups; and

which may be interrupted by a further oxygen or nitrogen atom;

with the proviso that at least one of the 4 C₁-C₄alkyl groups in ortho position to the nitrogen atom is higher alkyl than methyl;

L₁, L₂ and L₄ is a linking group selected from the group consisting of

a direct bond, R₁-Y or R₂-C(O)-Y- where Y is attached to G₁ and/or G₂; C₁-C₂₅alkylene,

C₂-C₂₅alkylene interrupted by -O-, -S-, -SO-, -SO₂-, >N-R_3 , $\text{--}\overset{\text{O}}{\parallel}\text{C--}$,

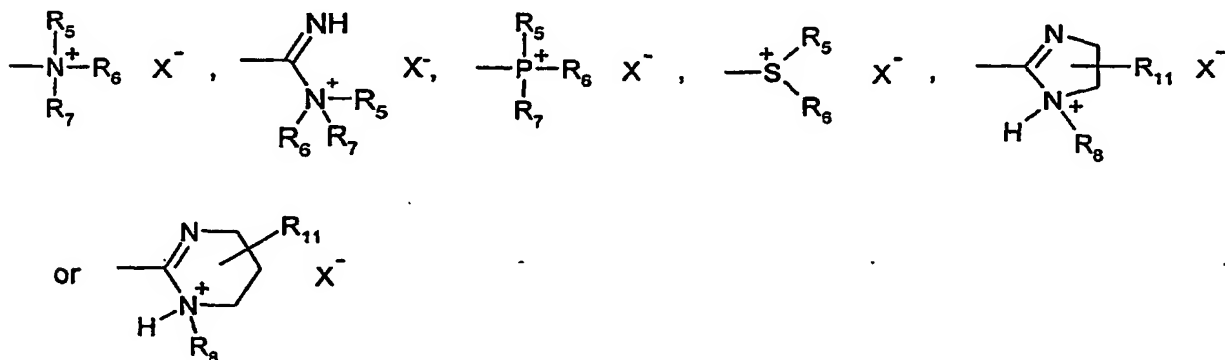
$\text{--}\overset{\text{O}}{\parallel}\text{C--O--}$, $\text{--}\overset{\text{O}}{\parallel}\text{C--N--R}_4$, phenylene or C₅-C₈cycloalkylene;

Y is O, or NR₉

L₃ is a group containing at least one carbon atom and is such that the radical •L₃-(Q⁺X⁻) derived from the group is able to initiate polymerization of ethylenically unsaturated monomers;

Q₂ is a direct bond, O, NR₅ or NR₅R₆;

Q⁺ is a cationic group selected from the group consisting of



wherein

R₁ is C₁-C₁₈alkylene,

R₂ is a direct bond or C₁-C₁₈alkylene,

R₃ is hydrogen or C₁-C₈alkyl,

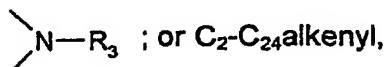
R₄ is hydrogen or C₁-C₄alkyl,

R₅, R₆ and R₇ are each independently of the others hydrogen, C₁-C₁₈alkyl,

C₃-C₁₂cycloalkyl, phenyl or C₇-C₉phenylalkyl or C₆-C₁₀heteroaryl which all may be unsubstituted or substituted by halogen, OH, NO₂, CN, C₁-C₄alkoxy, or

R₅, R₆ and R₇ together with the nitrogen to which they are bonded form a 3-12 membered monocyclic or polycyclic ring, which may contain further heteroatoms;

R₈ is hydrogen or C₁-C₂₅alkyl, C₃-C₂₅alkyl interrupted by oxygen, sulfur or by



R₉ is hydrogen, C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkinyl, phenyl, C₇-C₉phenylalkyl, which all may be unsubstituted or substituted by one or more hydroxy, halogen or C₁-C₄alkoxy groups;

R₁₁ is hydrogen or C₁-C₁₈alkyl;

R₂₂ is C₁-C₁₈alkyl;

X⁻ is the anion of a C₁-C₁₈carboxylic acid which may contain more than one carboxylic acid group, fluoride, chloride, bromide, iodide, nitrite, nitrate, hydroxide, acetate, hydrogen sulfate, sulfate, C₁-C₁₈alkoxy sulfate, aromatic or aliphatic sulfonate, carbonate, hydrogen carbonate, perchlorate, chlorate, tetrafluoroborate, borate, phosphate, hydrogenphosphate, dihydrogenphosphate or mixtures thereof; and p, q, and r are independently of each other a number from 0 to 10 and at least one is different from 0.

Alkyl having up to 18 carbon atoms is a branched or unbranched radical, for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

C₃-C₁₈Alkyl interrupted by oxygen, sulfur or by >N-R_3 is, for example, CH₃-O-CH₂CH₂-

CH₃-S-CH₂CH₂-, CH₃-N(CH₃)-CH₂CH₂-, CH₃-O-CH₂CH₂-O-CH₂CH₂-,
CH₃-(O-CH₂CH₂)₂O-CH₂CH₂-, CH₃-(O-CH₂CH₂)₃O-CH₂CH₂- or
CH₃-(O-CH₂CH₂)₄O-CH₂CH₂-.

C₇-C₉Phenylalkyl is, for example, benzyl, α-methylbenzyl, α, α -dimethylbenzyl or 2-phenylethyl. Preference is given to benzyl and α,α-dimethylbenzyl.

C₁-C₂₅Alkylene is a branched or unbranched radical, for example methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene, dodecamethylene or octadecamethylene.

C₂-C₂₅alkylene interrupted by -O-, -S-, -SO-, -SO₂-, >N-R_3 , $\text{—}\overset{\text{O}}{\parallel}\text{C—}$, $\text{—}\overset{\text{O}}{\parallel}\text{C—O—}$,

$\text{—}\overset{\text{O}}{\parallel}\text{C—N—}$ $\begin{array}{c} | \\ \text{R}_4 \end{array}$, phenylene or C₅-C₈cycloalkylene is, for example,

-CH₂-O-CH₂-, -CH₂-S-CH₂-, -CH₂-N(CH₃)-CH₂-, -CH₂-O-CH₂CH₂-, -CH₂CH₂-O-CH₂CH₂-,
-CH₂CH₂-O-CH₂CH₂-O-CH₂CH₂-, -CH₂CH₂-(O-CH₂CH₂)₂O-CH₂CH₂-,
-CH₂CH₂-(O-CH₂CH₂)₃O-CH₂CH₂-, -CH₂CH₂-(O-CH₂CH₂)₄O-CH₂CH₂-

-CH₂CH₂-S-CH₂CH₂-, $\text{—CH}_2\text{—CH}_2\text{—}\overset{\text{O}}{\parallel}\text{C—NH—(CH}_2\text{)}_3\text{—}$, $\text{—CH}_2\text{—CH}_2\text{—}\overset{\text{O}}{\parallel}\text{C—NH—(CH}_2\text{)}_6\text{—}$,

$\text{—CH}_2\text{—CH}_2\text{—}\langle \bigcirc \rangle\text{—CH}_2\text{—CH}_2\text{—}$ or $\text{—CH}_2\text{—CH}_2\text{—}\langle \bigcirc \rangle\text{—CH}_2\text{—CH}_2\text{—}$.

Alkenyl having 2 to 24 carbon atoms is a branched or unbranched radical such as, for example, vinyl, propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, oleyl, n-2-octadecenyl or n-4-octadecenyl. Preference is given to alkenyl having 3 to 18, especially 3 to 12, for example 3 to 6, especially 3 to 4 carbon atoms.

Alkynyl having from 3 to 18 carbon atoms is a branched or unbranched radical, for example propynyl, 2-butylnyl, 3-butylnyl, isobutylnyl, n-2,4-pentadiynyl, 3-methyl-2-butylnyl, n-2-octynyl, n-2-dodecynyl, isododecynyl.

Halogen is, for example, chlorine, bromine or iodine. Preference is given to chlorine and bromine.

Alkoxy having up to 25 carbon atoms is a branched or unbranched radical, for example methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, pentyloxy, isopentyloxy, hexyloxy, heptyloxy, octyloxy, decyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy. Preference is given to alkoxy having from 1 to 12, especially from 1 to 8, e.g. from 1 to 6, carbon atoms.

Alkanoyloxy having up to 25 carbon atoms is a branched or unbranched radical, for example acetoxyl, propionyl, butanoyloxy, pentanoyloxy, hexanoyloxy, heptanoyloxy, octanoyloxy, nonanoyloxy, decanoyloxy, undecanoyloxy, dodecanoyloxy, tridecanoyloxy, tetradecanoyloxy, pentadecanoyloxy, hexadecanoyloxy, heptadecanoyloxy, octadecanoyloxy, icosanoyloxy or docosanoyloxy. Preference is given to alkanoyloxy having from 2 to 18, especially from 2 to 12, e.g. from 2 to 6, carbon atoms.

Hydroxyl-substituted C_2-C_{18} alkyl is a branched or unbranched radical which contains preferably 1 to 3, in particular 1 or 2, hydroxyl groups, such as, for example, hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 4-hydroxybutyl, 3-hydroxybutyl, 2-hydroxybutyl, 5-hydroxypentyl, 4-hydroxypentyl, 3-hydroxypentyl, 2-hydroxypentyl, 6-hydroxyhexyl, 5-hydroxyhexyl, 4-hydroxyhexyl, 3-hydroxyhexyl, 2-hydroxyhexyl, 7-hydroxyheptyl, 6-hydroxyheptyl, 5-hydroxyheptyl, 4-hydroxyheptyl, 3-hydroxyheptyl, 2-hydroxyheptyl, 8-hydroxyoctyl, 7-hydroxyoctyl, 6-hydroxyoctyl, 5-hydroxyoctyl, 4-hydroxyoctyl, 3-hydroxyoctyl, 2-hydroxyoctyl, 9-hydroxynonyl, 10-hydroxydecyl, 11-hydroxyundecyl, 12-hydroxydodecyl, 13-hydroxytridecyl, 14-hydroxytetradecyl, 15-hydroxypentadecyl, 16-hydroxyhexadecyl, 17-hydroxyheptadecyl, 18-hydroxyoctadecyl.

C_5-C_{12} cycloalkyl is for example cyclopentyl, cyclohexyl, cycloheptyl, methylcyclopentyl or cyclooctyl.

If X^\cdot is a monovalent radical of a saturated, unsaturated or aromatic carboxylic acid, it is, for example, an acetyl, caproyl, stearoyl, acryloyl, methacryloyl, benzoyl or β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl radical.

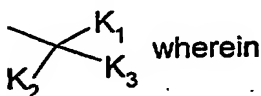
If X^\cdot is a divalent radical of a dicarboxylic acid, it is, for example, a malonyl, succinyl, glutaryl, adipoyl, suberoyl, sebacoyl, maleoyl, itaconyl, phthaloyl, dibutylmalonyl, dibenzylmalonyl, butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonyl or bicycloheptenedicarbonyl radical.

If X^\cdot is a trivalent radical of a tricarboxylic acid, it is, for example, a trimellitoyl, citryl or nitrilotriacetyl radical.

Heteroaryl is for example pyryl, thiophenyl, furyl, pyridyl or pyrimidyl.

When R_5 , R_6 and R_7 form a monocyclic or polycyclic heterocyclic ring, the resulting cation is for example a pyridinium, quinolinium, isoquinolinium, imidazolium or thiazolium cation.

In one embodiment of the instant invention in formula I or II $-L_1(Q^+X^-)$, $-L_2(Q^+X^-)$, and $-L_3(Q^+X^-)$, are a group



K_1 and K_2 are hydrogen, C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl and

K_3 is a group $-COK_4$ or $-\text{C}_6\text{H}_4-Z-K_5$ where

K_4 is $-Y-[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-$ or $-Y-CH_2-CHOH-CH_2-N^+R_5R_6X^- - \{[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-\}_u$, where s is a number 0-8, t is a number 0-4 and u is 0 or 1 and Y is $-O-$ or $-NR_9$; or

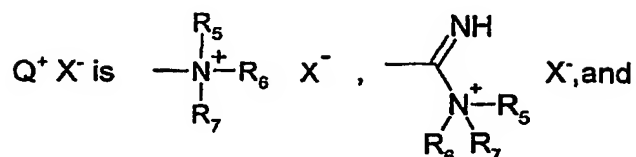
K_4 is a group $-Y-\text{C}_6\text{H}_4-Q^+X^-$, $-Y-\text{C}_5\text{H}_4-N^+R_5X^-$ or $-N\text{C}_4\text{H}_8-N^+(R_5)(R_6)X^-$ or

Z is $-C(O)-$ or a direct bond,

if Z is $-C(O)-$, K_5 has the same meaning as K_4 ,

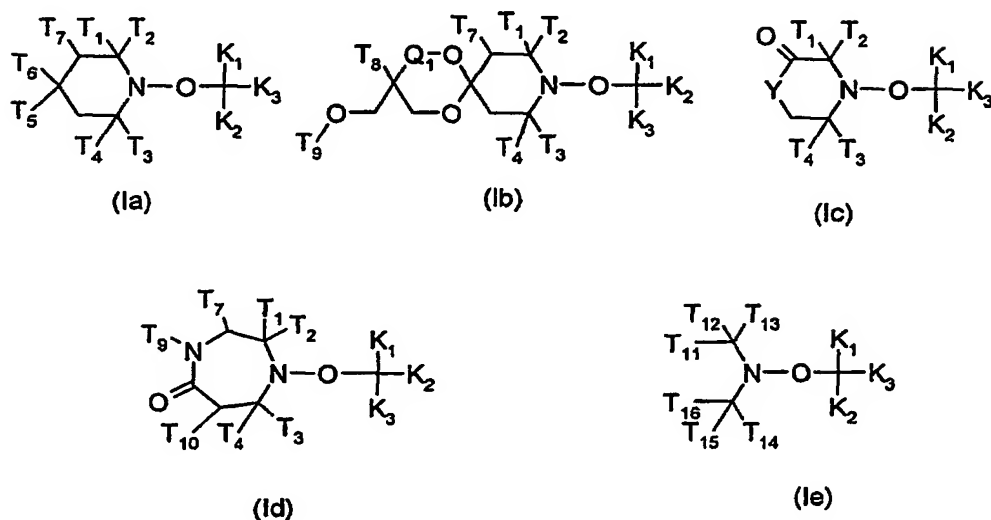
if Z is a direct bond, K_5 is $Y-CH_2-CHOH-CH_2-N^+R_5R_6X^- - \{[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-\}_u$, Q^+X^- , $-CH_2Q^+X^-$ or $-CHCH_3Q^+X^-$;

and Y is -O- or -NR₉ or a direct bond;



the other substituents are as defined above.

Preferably the compounds are of formulae Ia, Ib, Ic, Id or Ie



wherein

Q₁ is a direct bond or a -CH₂- group;

if Q₁ is a direct bond, T₈ is hydrogen,

if Q₁ is -CH₂-, T₈ is methyl or ethyl;

T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;

T₇ and T₁₀ are independently hydrogen or methyl;

T₅ and T₆ are hydrogen or

T₅ and T₆ together are a group =O, =NOH, =NO-T₉ or

T₅ is hydrogen and T₆ is -O-T₉ or -NR₉-T₉ where T₉ is hydrogen, R₉ or -C(O)-R₉, where R₉ is hydrogen, C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkynyl, phenyl, C₇-C₉phenylalkyl, which may be unsubstituted or substituted by one or more hydroxy, halogen or C₁-C₄alkoxy groups;

T₁₁, T₁₂, T₁₃, T₁₄, T₁₅ and T₁₆ independently are C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkinyl, C₅-C₁₂cycloalkyl, phenyl or C₇-C₉phenylalkyl; or

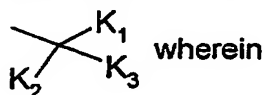
T₁₁ is hydrogen and T₁₂ is a group -P(O)(OC₂H₅)₂ and the others are as defined above; or

or T₁₁ and T₁₄ are a group -CH₂-O-T₉ and the others are as defined above; or

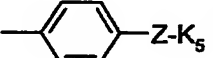
T₁₆ is a group -C(O)-Y-R₅ and the others are as defined above; or

T₁₁, T₁₂ and T₁₃ are a group -CH₂OH;

-L₃(Q⁺X⁻), is a group




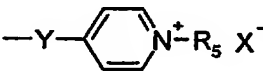
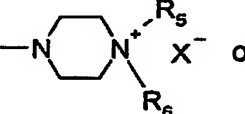
K₁ and K₂ are hydrogen, C₅-C₁₂cycloalkyl, phenyl or C₇-C₉phenylalkyl and

K₃ is a group -COK₄ or -Z-K₅ where

K₄ is Y-[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻ or

-Y-CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ X⁻R₅R₆]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u,

where s and t is a number 0-4 and u is 0 or 1; or

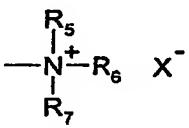
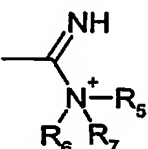
K₄ is a group ,  or  or

Z is -C(O)- or a direct bond,

if Z is -C(O)- K₅ has the meaning of K₄,

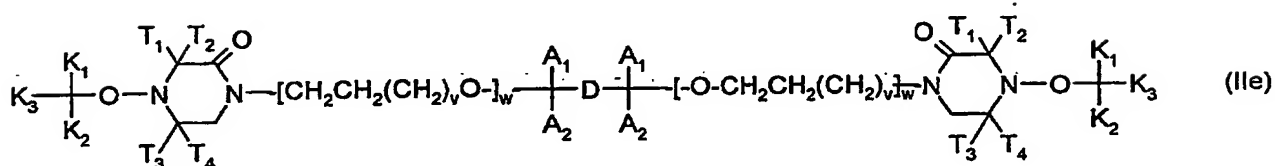
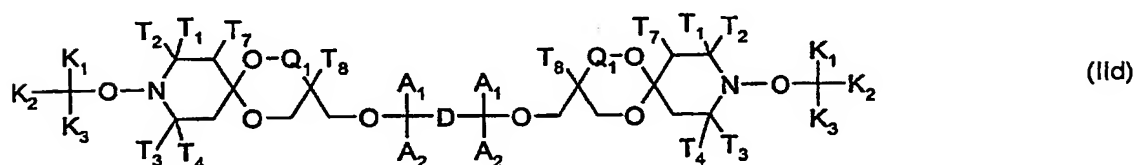
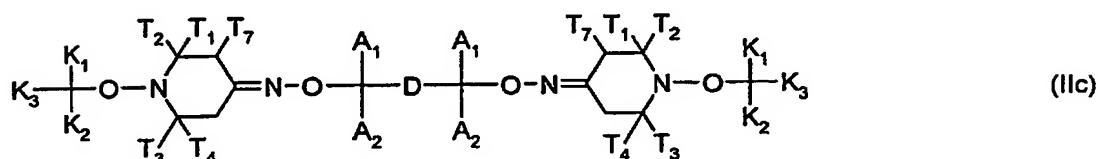
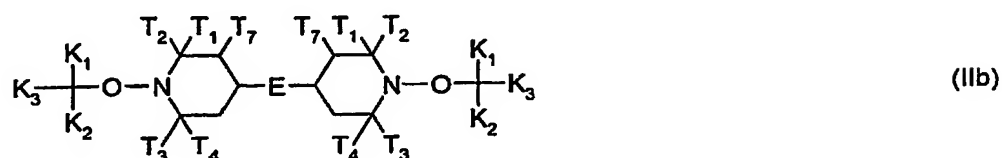
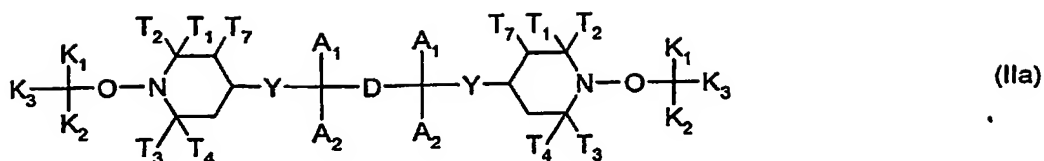
if Z is a direct bond, K₅ is O-CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u, Q⁺X⁻, -CH₂Q⁺X⁻ or -CHCH₃Q⁺X⁻;

Y is -O- or -NR₉;

Q⁺X⁻ is  X⁻,  X⁻, and

X⁻ and the other substituents are as defined above.

In another preferred embodiment of the invention the compounds are of formula IIa, IIb, IIc, IIId or IIe

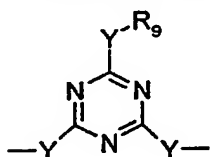


wherein

A_1 and A_2 are independently hydrogen or together with the carbon atom to which they are bonded form a carbonyl group, $-\text{C}(\text{O})-$;

D is a direct bond or C_1 - C_{12} alkylene, C_1 - C_{12} alkylene which is interrupted by one or more O , S , or NR_9 atoms, C_5 - C_{12} cycloalkylene or phenylene;

E is a group $-\text{NR}_9-(\text{CH}_2)_x-\text{NR}_9-$ where x is a number from 2 to 12 or a group



v is a number from 0 to 10 and w is 0 or 1;

Q_1 is a direct bond or a $-CH_2-$ group;

if Q_1 is a direct bond, T_8 is hydrogen,

if Q_1 is $-CH_2-$, T_8 is hydrogen, methyl or ethyl;

Y is $-O-$ or $-NR_9$;

T_1, T_2, T_3 and T_4 are independently methyl or ethyl with the proviso that at least one is ethyl;

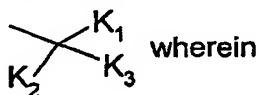
T_7 is hydrogen or methyl;

T_5 and T_6 are hydrogen or

T_5 and T_6 together are a group $=O, =NOH, =NO-T_9$ or

T_5 is hydrogen and T_6 is $-O-T_9$ or $-NR_9-T_9$ where T_9 is hydrogen, R_9 or $-C(O)-R_9$, where R_9 is hydrogen, C_1-C_{18} alkyl, C_3-C_{18} alkenyl, C_3-C_{18} alkinyl, phenyl, C_7-C_9 phenylalkyl, which may be unsubstituted or substituted by one or more hydroxy, halogen or C_1-C_4 alkoxy groups;

$-L_3(Q^+X^-)$, is a group



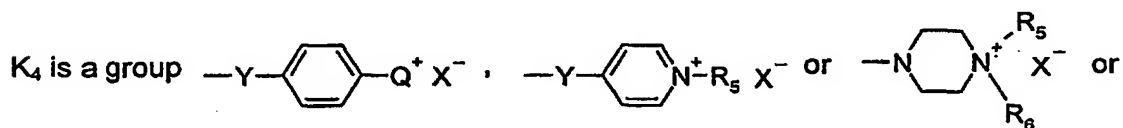
K_1 and K_2 are hydrogen, C_5-C_{12} cycloalkyl, phenyl or C_7-C_9 phenylalkyl and

K_3 is a group $-COK_4$ or $-\text{C}_6\text{H}_4-Z-K_5$ where

K_4 is $Y-[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_r-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-$ or

$-Y-CH_2-CHOH-CH_2-N^+R_5R_6X^--[[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_r-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-]_u$,

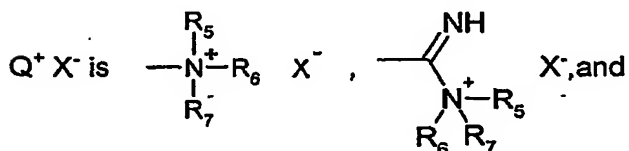
where s and t is a number 0-4 and u is 0 or 1; or



Z is $-C(O)-$ or a direct bond,

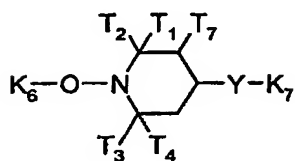
if Z is $-C(O)-$ K_5 has the meaning of K_4 ,

if Z is a direct bond, K_5 is $O-CH_2-CHOH-CH_2-N^+R_5R_6X^--[[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_r-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-]_u$, Q^+X^- , $-CH_2Q^+X^-$ or $-CHCH_3Q^+X^-$;

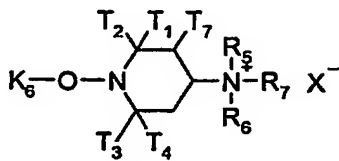


X^- and the other substituents are as defined above.

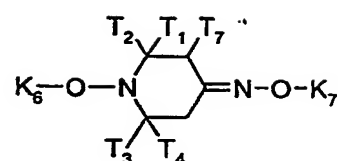
Also preferred are the compounds of formula IIIa, IIIb, IIIc, IIId or IIIe



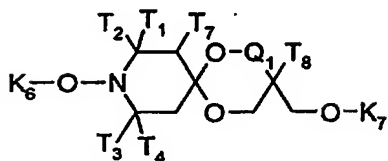
(IIIa)



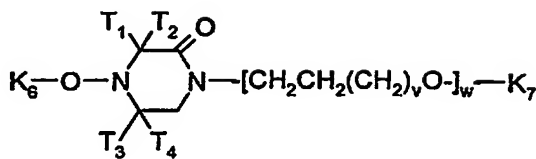
(IIIb)



(IIIc)



(IIId)



(IIIe)

T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;

T₇ is hydrogen or methyl;

Y is O or NR₉;

Q₁ is a direct bond or a -CH₂- group;

if Q₁ is a direct bond, T₈ is hydrogen,

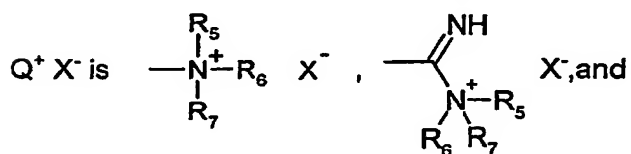
if Q₁ is -CH₂-, T₈ is methyl or ethyl;

v is a number from 0 to 10 and w is 0 or 1;

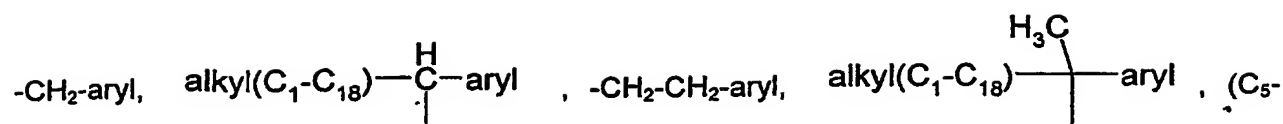
K₇ is a group -CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻ -{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u,

where s and t is a number 0-4 and u is 0 or 1; or a group -D₁- Q⁺ X⁻ where

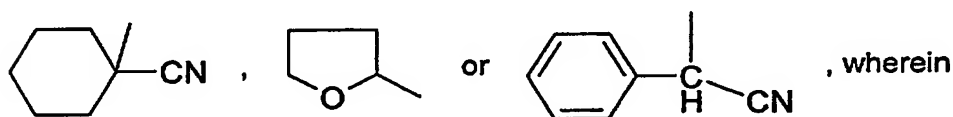
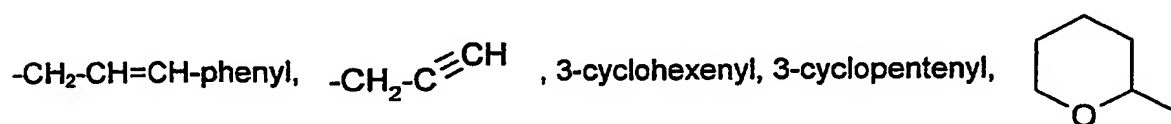
D₁ is C₁-C₁₂alkylene, C₁-C₁₂alkylene which is interrupted by one or more O, S, or NR₉ atoms, C₆-C₁₂cycloalkylene or phenylene;



K₆ is selected from the group consisting of



$\text{C}_6\text{cycloalkyl})_2\text{CCN}$, $(\text{C}_1\text{-C}_{12}\text{alkyl})_2\text{CCN}$, $-\text{CH}_2\text{CH=CH}_2$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-C(O)-}(\text{C}_1\text{-C}_{12})\text{alkyl}$,
 $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-C(O)-}(\text{C}_6\text{-C}_{10})\text{aryl}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-C(O)-}(\text{C}_1\text{-C}_{12})\text{alkoxy}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-}$
 $\text{CR}_{30}\text{-C(O)-phenoxy}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-C(O)-N-di}(\text{C}_1\text{-C}_{12})\text{alkyl}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-CO-}$
 $\text{NH}(\text{C}_1\text{-C}_{12})\text{alkyl}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-CO-NH}_2$, $-\text{CH}_2\text{CH=CH-CH}_3$, $-\text{CH}_2\text{-C(CH}_3\text{)=CH}_2$,



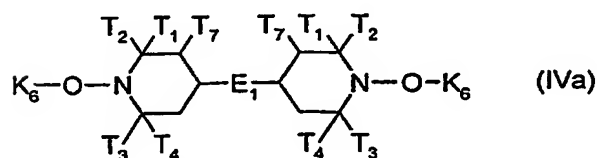
R_{30} is hydrogen or $\text{C}_1\text{-C}_{12}\text{alkyl}$;

the alkyl groups are unsubstituted or substituted with one or more $-\text{OH}$, $-\text{COOH}$ or $-\text{C(O)R}_{30}$ groups; and

the aryl groups are phenyl or naphthyl which are unsubstituted or substituted with $\text{C}_1\text{-C}_{12}\text{alkyl}$, halogen, $\text{C}_1\text{-C}_{12}\text{alkoxy}$, $\text{C}_1\text{-C}_{12}\text{alkylcarbonyl}$, glycidyloxy, OH , $-\text{COOH}$ or $-\text{COO}(\text{C}_1\text{-C}_{12})\text{alkyl}$ and

X^* and the other substituents are as defined above.

Particularly suitable are the compounds according to formula IVa



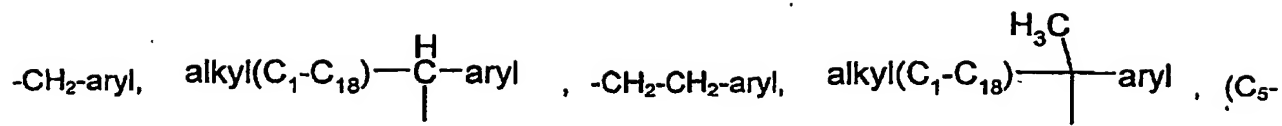
wherein

T_1 , T_2 , T_3 and T_4 are independently methyl or ethyl with the proviso that at least one is ethyl;

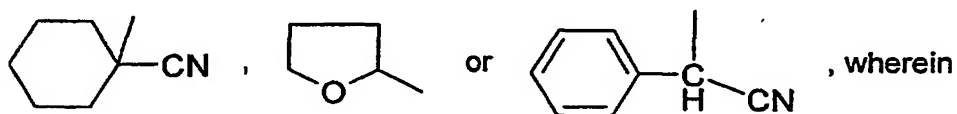
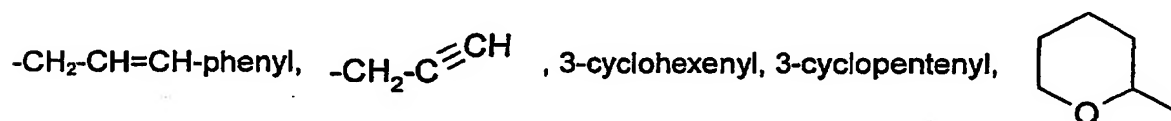
T_7 is hydrogen or methyl;

E_1 is $-\text{N}^+ \text{X}^- \text{R}_5\text{R}_6\text{-(CH}_2\text{)}_x\text{-N}^+ \text{X}^- \text{R}_5\text{R}_6$ where x is a number from 2 to 12;

K_6 is selected from the group consisting of



$\text{C}_6\text{cycloalkyl})_2\text{CCN}$, $(\text{C}_1\text{-C}_{12}\text{alkyl})_2\text{CCN}$, $-\text{CH}_2\text{CH=CH}_2$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-C(O)-}(\text{C}_1\text{-C}_{12})\text{alkyl}$,
 $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-C(O)-}(\text{C}_6\text{-C}_{10})\text{aryl}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{20}\text{-C(O)-}(\text{C}_1\text{-C}_{12})\text{alkoxy}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-}$
 $\text{CR}_{30}\text{-C(O)-phenoxy}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-C(O)-N-di}(\text{C}_1\text{-C}_{12})\text{alkyl}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-CO-}$
 $\text{NH}(\text{C}_1\text{-C}_{12})\text{alkyl}$, $(\text{C}_1\text{-C}_{12})\text{alkyl-CR}_{30}\text{-CO-NH}_2$, $-\text{CH}_2\text{CH=CH-CH}_3$, $-\text{CH}_2\text{-C}(\text{CH}_3)=\text{CH}_2$,



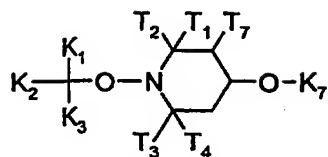
R_{30} is hydrogen or $\text{C}_1\text{-C}_{12}\text{alkyl}$;

the alkyl groups are unsubstituted or substituted with one or more $-\text{OH}$, $-\text{COOH}$ or $-\text{C(O)R}_{30}$ groups; and

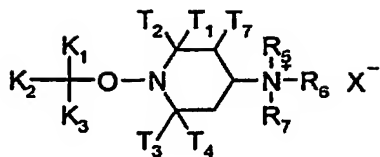
the aryl groups are phenyl or naphthyl which are unsubstituted or substituted with $\text{C}_1\text{-C}_{12}\text{alkyl}$, halogen, $\text{C}_1\text{-C}_{12}\text{alkoxy}$, $\text{C}_1\text{-C}_{12}\text{alkylcarbonyl}$, glycidyloxy, OH , $-\text{COOH}$ or $-\text{COO}(\text{C}_1\text{-C}_{12})\text{alkyl}$ and

X^* and the other substituents are as defined above.

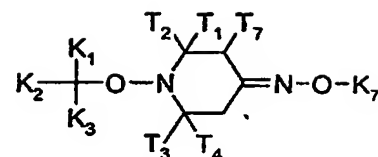
Preference is also given to compounds of formula Va, Vb, Vc, Vd or Ve



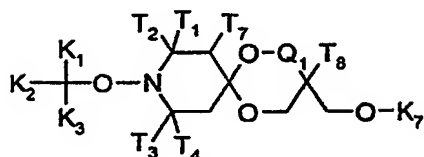
(Va)



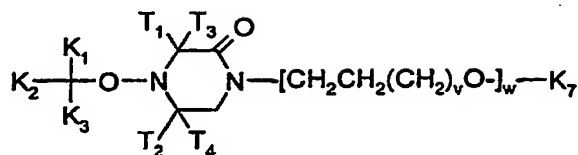
(Vb)



(Vc)



(Vd)



(Ve)

wherein

T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;

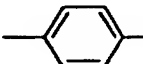
T₇ is hydrogen or methyl;

Q₁ is a direct bond or a -CH₂- group;

if Q₁ is a direct bond, T₈ is hydrogen,

if Q₁ is -CH₂-, T₈ is methyl or ethyl;

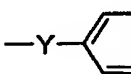
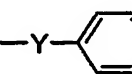
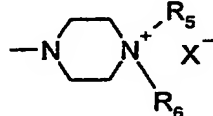
K₁ and K₂ are hydrogen, C₅-C₁₂cycloalkyl, phenyl or C₇-C₉phenylalkyl and

K₃ is a group -COK₄ or -Z-K₅ where

K₄ is Y-[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻ or

-Y-CH₂-CHOH-CH₂-N⁺ R₅R₆X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u,

where s and t is a number 0-4 and u is 0 or 1; or

K₄ is a group -Q⁺ X⁻, -N⁺ R₅ X⁻ or -N⁺ R₅ R₆ X⁻ or

Z is -C(O)- or a direct bond,

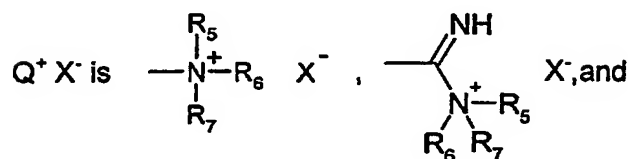
if Z is -C(O)- K₅ has the meaning of K₄,

if Z is a direct bond, K₅ is O-CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u, Q⁺X⁻, -CH₂Q⁺X⁻ or -CHCH₃Q⁺X⁻;

K₇ is a group -CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u,

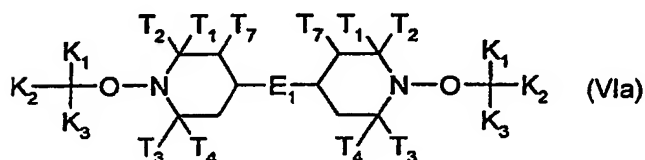
where s and t is a number 0-4 and u is 0 or 1; or a group -D₁- Q⁺ X⁻ where

D₁ is C₁-C₁₂alkylene, C₁-C₁₂alkylene which is interrupted by one or more O, S, or NR₉ atoms, C₅-C₁₂cycloalkylene or phenylene;



X⁻ and the other substituents are as defined above.

Also preferred are compounds of formula VIa



wherein

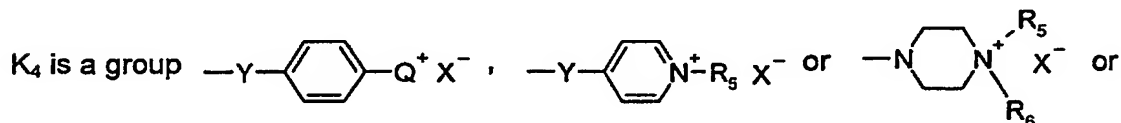
T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;
T₇ is hydrogen or methyl;

E₁ is -N⁺ X⁻ R₅R₆⁻(CH₂)_x-N⁺ X⁻ R₅R₆ where x is a number from 2 to 12;

K₁ and K₂ are hydrogen, C₅-C₁₂cycloalkyl, phenyl or C₇-C₉phenylalkyl and

K₃ is a group -COK₄ or $\text{---} \text{C}_6\text{H}_4 \text{---} Z \text{---} K_5$ where

K₄ is Y-[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻ or
-Y-CH₂-CHOH-CH₂-N⁺ R₅R₆X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u,
where s and t is a number 0-4 and u is 0 or 1; or

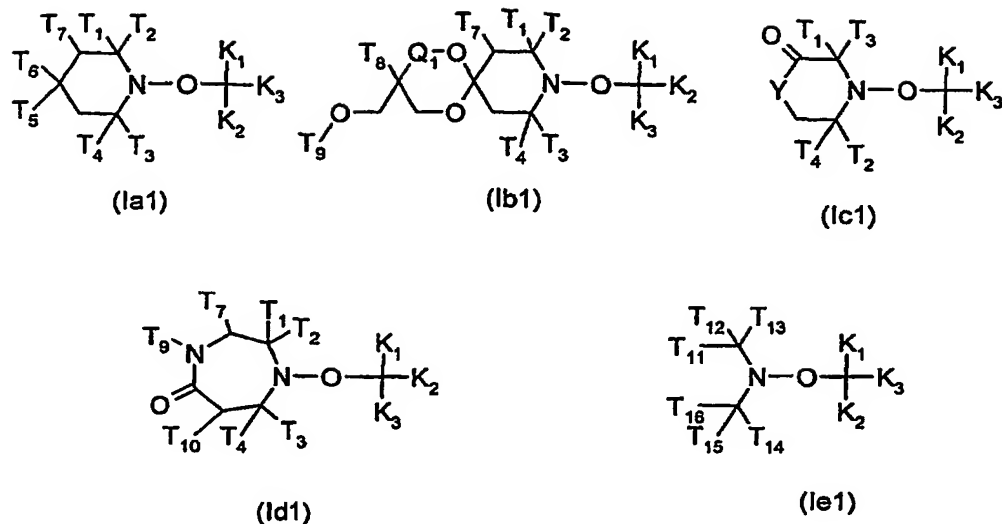


Z is -C(O)- or a direct bond,

if Z is -C(O)- K₅ has the meaning of K₄,

if Z is a direct bond, K₅ is O-CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u, Q⁺X⁻, -CH₂Q⁺X⁻ or -CHCH₃Q⁺X⁻ and
X⁻ and the other substituents are as defined above.

Of particular interest are compounds of formula Ia1, Ib1, Ic1, Id1 or Ie1



wherein

Q₁ is a direct bond or CH₂;

T₁, T₃ are ethyl and T₂, T₄ and T₇ are methyl;

if Q₁ is a direct bond, T₈ is H;

if Q₁ is CH₂, T₈ is methyl or ethyl;

T₁₀ is H if T₇ is methyl or T₁₀ is methyl if T₇ is H;

T₁₁, T₁₂, T₁₃, T₁₄, T₁₅ and T₁₆ are independently methyl or ethyl; or

T₁₁ is H, T₁₂ is isopropyl, T₁₃ is phenyl and T₁₄, T₁₅, T₁₆ are methyl; or

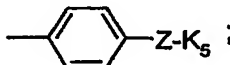
T₁₁ is H, T₁₂ is -P(=O)(OC₂H₅)₂, T₁₃ is t-butyl and T₁₄, T₁₅, T₁₆ are methyl; or

T₁₁ and T₁₄ are -CH₂O-T₉ and T₁₂, T₁₅ are methyl or phenyl and T₁₃, T₁₆ are methyl or ethyl; or

T₁₁, T₁₂, T₁₃, T₁₄, T₁₅ are methyl and T₁₆ is a group -CO-O-R₉ or -CON(R₉)₂; or

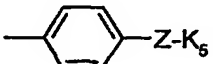
T₁₁, T₁₂ and T₁₃ are -CH₂OH, T₁₄ is H, T₁₅ is isopropyl and T₁₆ phenyl;

K₁ is H, K₂ is methyl or ethyl and

K₃ is a group -CO-K₄ or ; Z is -CO- or a direct bond;

K₄ is -Y-CH₂-CH₂-(CH₂)_s-N⁺X⁻R₅R₆R₇ or;

-Y-CH₂-CHOH-CH₂-N-CH₂-CH₂-(CH₂)_s-N⁺X⁻R₅R₆R₇ where Y is O or NR₉ and s is a number from 0 to 2;

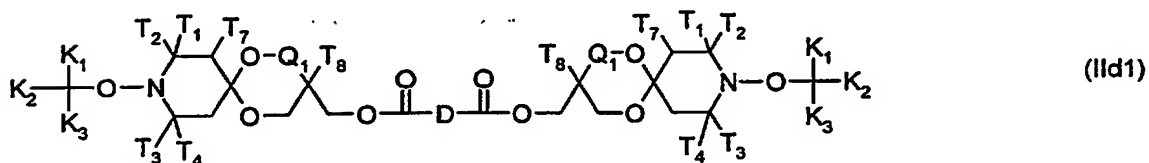
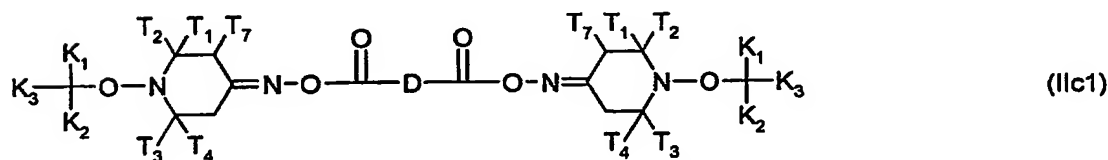
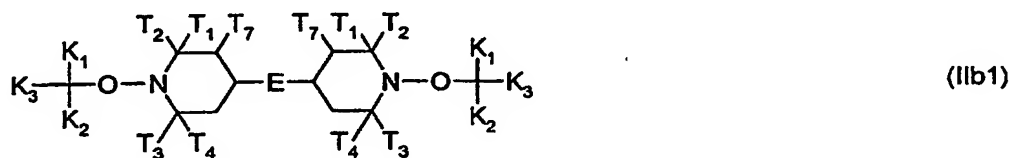
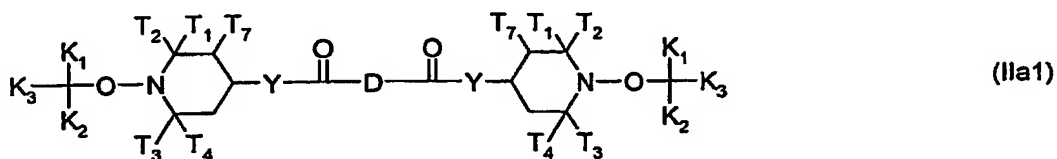
if K₃ is , Z is -CO- or a direct bond;

if Z is -CO-, K₅ has the same meaning as K₄;

if Z is a direct bond, K₅ is a group -O-CH₂-CHOH-CH₂-N-CH₂-CH₂-(CH₂)₉-N⁺X⁻R₅R₆R₇ or -CH₂N⁺R₅R₆R₇ X⁻ and

X⁻ and the other substituents are as defined above.

Also of particular interest are compounds of formula IIa1, IIb1, IIc1 or IId1



wherein

Q₁ is a direct bond or CH₂ ;

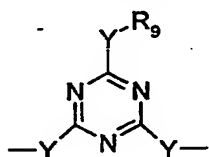
T₁, T₃ are ethyl and T₂, T₄ and T₇ are methyl;

if Q₁ is a direct bond, T₈ is H;

if Q₁ is CH₂, T₈ is methyl or ethyl;

D is a direct bond, C₁-C₁₂alkylene or phenylene;

E is -NR₅-(CH₂)_x-NR₅- where x is 2 to 12 or a group



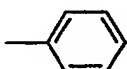
wherein Y is =NR₉

K_1 is H, K_2 is methyl or ethyl and

K_3 is a group $-\text{CO}-K_4$ or  $-\text{Z}-K_5$;

K_4 is $-\text{Y}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_s-\text{N}^+\text{X}^-\text{R}_5\text{R}_6\text{R}_7$ or;

$-\text{Y}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_s-\text{N}^+\text{X}^-\text{R}_5\text{R}_6\text{R}_7$ where Y is O or NR_9 and s is a number from 0 to 2;

if K_3 is  $-\text{Z}-K_5$, Z is $-\text{CO}-$ or a direct bond;

if Z is $-\text{CO}-$ K_5 has the same meaning as K_4 ;

if Z is a direct bond K_5 is a group $-\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_s-\text{N}^+\text{X}^-\text{R}_5\text{R}_6\text{R}_7$ or $-\text{CH}_2\text{N}^+\text{R}_5\text{R}_6\text{R}_7 \text{X}^-$;

and

X^- and the other substituents are as defined above.

The precursors of the above compounds can be prepared according to known methods.

The preparation of open chain alkoxyamines is for example described in WO 99/03894 or in WO 00/07981. Alkoxyamines based on tetraalkyl piperidine are for example described in GB 2 335 1290 or in GB 2 361 235. Further heterocyclic alkoxyamines are described in GB 2 342 649.

A very suitable, but not the only possible, method for the introduction of the cationic moiety into the molecule of the alkoxyamine consists of first preparing the suitable precursor alkoxyamine which is then quarternised. Examples of such Alkoxyamines are given in Table 1. The non cationic precursors can be prepared by a variety of methods described in the cited patents using the suitable building blocks bearing the appropriate nucleophilic groups capable of quarternisation. Few examples of such groups are primary, secondary or tertiary amine group, pyridyl, quinolyl, isoquinolyl, imidazolyl, thiazolyl groups, trialkyl or triaryl or alkylarylphosphine groups or a thioether group. These can be quarternised by a variety of electrophilic reagents, for example alkyl halides, alkyl sulfonates, alkyl carbonates, trialkyloxonium salts, epoxides or others. A special case is the formation of the cationic moiety by protonation of the cited nucleophilic groups by their protonation with acids.

A given specific anion of the cationic alkoxyamine can be exchanged against a different one using for example ion exchangers or well known ion metathesis.

A further aspect of the invention is a process for preparing a monomer/polymer clay nanocomposite dispersion comprising the steps of

- A) providing a first aqueous dispersion of a natural or synthetic clay which can be partially intercalated and/or exfoliated and wherein said clay has an exchangeable cation;
adding a compound according to claim 1 to said dispersion and exchanging said cation at least partially;
- B) adding to said dispersion at least one ethylenically unsaturated monomer and polymerizing at least a portion of said ethylenically unsaturated monomer.

Clay minerals are typically comprised of hydrated aluminum silicates that are fine-grained and have a platy habit. The crystalline structure of a typical clay mineral is a multi-layered structure comprised of combinations of layers of SiO_4 tetrahedra that are joined to layers of $\text{AlO}(\text{OH})_2$ octahedra. A so called "gallery" is formed which describes the defined interlayer spaces of the layered clay minerals. Depending of the clay mineral the gallery may contain water and/or other constituents such as potassium, sodium or calcium cations. Clay minerals vary based upon the combination their constituent layers and cations. Isomorphic substitution of the cations of clay mineral, such as Al^{3+} or Fe^{3+} substituting for the Si^{4+} ions in the tetrahedral network, or Al^{3+} , Mg^{2+} or Fe^{2+} substituting for other cations in the octahedral network, typically occurs and may impart a net negative charge on the clay structure. Natural occurring elements within the gallery of the clay, such as water molecules or sodium or potassium cations, are attracted to the surface of the clay layers due to this net charge.

Nanocomposites are compositions in which at least one of its constituents has one or more dimensions, such as length, width or thickness in the nanometer size range. The term nanocomposite, as used herein, denotes the state of matter wherein polymer molecules exist among at least partially exfoliated clay layers.

The term "intercalated nanocomposite", as used herein describes a nanocomposite that contains a regular insertion between the clay layers.

The term "exfoliated nanocomposite" as used herein describes a nanocomposite wherein the 1 nm thick layers of clay are dispersed in the matrix (oligomer/polymer) forming a composite structure on the nano/micro scale.

The clay minerals are items of commerce and are for example supplied by Süd-Chemie Inc., Germany.

Preferably the ethylenically unsaturated monomer or oligomer is selected from the group consisting of ethylene, propylene, n-butylene, i-butylene, styrene, substituted styrene, conjugated dienes, acrolein, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles, (alkyl)acrylamides, vinyl halides or vinylidene halides.

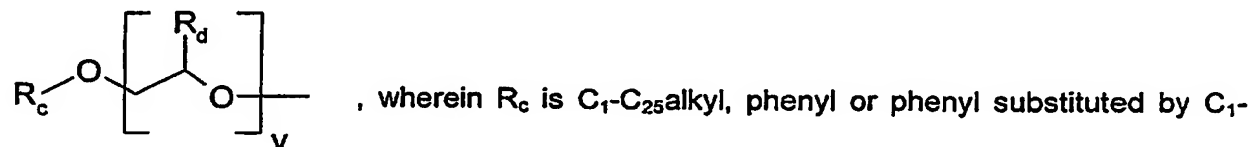
Particularly the ethylenically unsaturated monomers are ethylene, propylene, n-butylene, i-butylene, isoprene, 1,3-butadiene, α -C₅-C₁₈alkene, styrene, α -methyl styrene, p-methyl styrene or a compound of formula $\text{CH}_2=\text{C}(\text{R}_a)-(\text{C}=\text{Z})-\text{R}_b$, wherein R_a is hydrogen or C₁-C₄alkyl, R_b is NH_2 , $\text{O}^-(\text{Me}^+)$, glycidyl, unsubstituted C₁-C₁₈alkoxy, C₂-C₁₀₀alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted C₁-C₁₈alkoxy, unsubstituted C₁-C₁₈alkylamino, di(C₁-C₁₈alkyl)amino, hydroxy-substituted C₁-C₁₈alkylamino or hydroxy-substituted di(C₁-C₁₈alkyl)amino, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$ or $-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}^+\text{H}(\text{CH}_3)_2 \text{An}^-$;

An^- is a anion of a monovalent organic or inorganic acid;

Me is a monovalent metal atom or the ammonium ion.

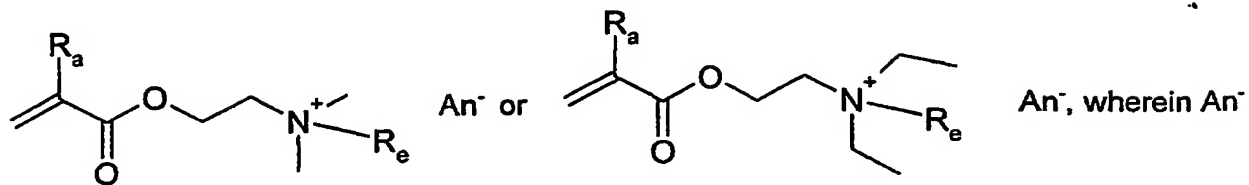
Z is oxygen or sulfur.

Examples for R_a as C₂-C₁₀₀alkoxy interrupted by at least one O atom are of formula



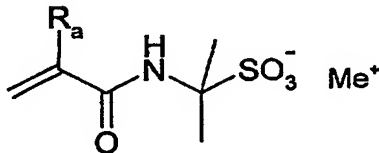
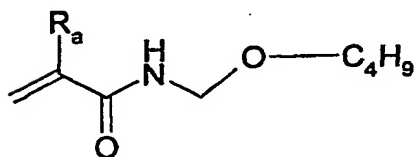
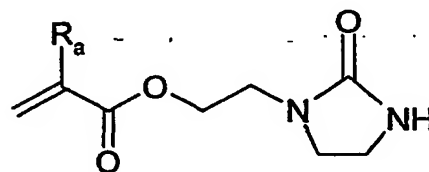
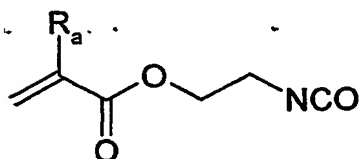
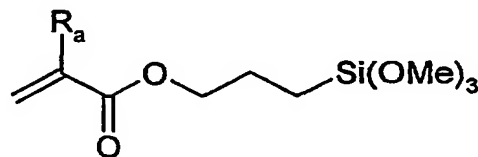
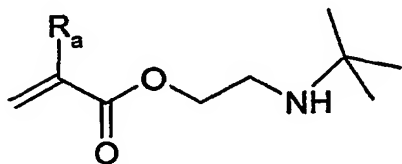
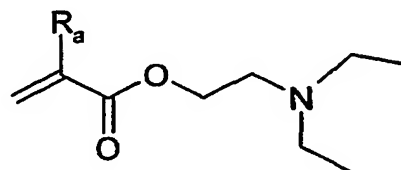
C₁₈alkyl, R_d is hydrogen or methyl and v is a number from 1 to 50. These monomers are for example derived from non ionic surfactants by acrylation of the corresponding alkoxyated alcohols or phenols. The repeating units may be derived from ethylene oxide, propylene oxide or mixtures of both.

Further examples of suitable acrylate or methacrylate monomers are given below.

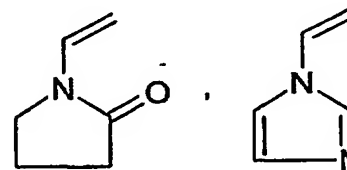


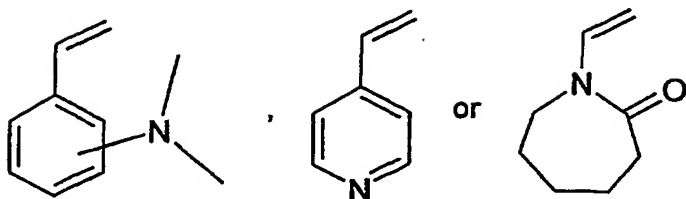
and R_a have the meaning as defined above and R_e is methyl or benzyl. An^- is preferably Cl^- , Br^- or $^-\text{O}_3\text{S}-\text{CH}_3$.

Further acrylate monomers are



Examples for suitable monomers other than acrylates are





Preferably R_a is hydrogen or methyl, R_b is NH_2 , glycidyl, unsubstituted or with hydroxy substituted C_1 - C_4 alkoxy, unsubstituted C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, hydroxy-substituted C_1 - C_4 alkylamino or hydroxy-substituted di(C_1 - C_4 alkyl)amino; and Z is oxygen.

Also suitable ethylenically unsaturated monomers are styrene, methylacrylate, ethylacrylate, butylacrylate, isobutylacrylate, tert. butylacrylate, hydroxyethylacrylate, hydroxypropylacrylate, dimethylaminoethylacrylate, glycidylacrylates, methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, glycidyl(meth)acrylates, acrylonitrile, acrylamide, methacrylamide or dimethylaminopropyl-methacrylamide.

Preferred is a process wherein the ethylenically unsaturated monomer is selected from the group consisting of C_1 - C_{18} alkyl methacrylate, C_1 - C_{18} alkyl acrylate, 2-ethylhexyl (meth)acrylate, isobornyl (meth)acrylate, lauryl (meth)acrylate, allyl (meth)acrylate, stearyl (meth)acrylate, acrylic acid, itaconic acid, methacrylic acid, butadiene, vinyl acetate, vinyl versate, styrene, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, vinyl aromatic monomers, divinylbenzene, divinylpyridine, divinyltoluene, diallyl phthalate, ethylene glycol di(meth)acrylate, butylene glycol di(meth)acrylate, divinylxylene, divinylethylbenzene, divinylsulfone, divinylketone, divinylsulfide, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl carbonate, diallyl malonate, diallyl oxalate, diallyl adipate, diallyl sebacate, divinyl sebacate, diallyl tartrate, diallyl silicate, triallyl tricarballate, triallyl aconitate, triallyl citrate, triallyl phosphate, N,N-methylene dimethacrylamide, N,N-methylene dimethacrylamide, N,N-ethylenediacylamide, trivinylbenzene, and the polyvinyl ethers of glycol, glycerol, pentaerythritol, resorcinol, monothio and dithio derivatives of glycols, and combinations thereof.

Special preference is given to a process wherein an acid containing unsaturated monomer is

added, which is selected from the group consisting of methacrylic anhydride, maleic anhydride, itaconic anhydride, acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acryloxypropionic acid, (meth)acryloxypropionic acid, styrene sulfonic acid, ethylmethacrylate-2-sulphonic acid, 2-acrylamido-2-methylpropane, sulphonic acid; phosphoethylmethacrylate; the corresponding salts of the acid containing monomer, and combinations thereof.

In one embodiment of the invention the process is carried out wherein the water phase of step A) is at least partially removed before performing step B).

It is also possible that in step B) an organic solvent is additionally added.

Preferred is a process wherein the polymerization is carried out by applying heat, at a temperature of from 60° C to 160° C.

Preferred is a process wherein the compound of formula I or II is added in an amount of from 1% to 100% by weight, based on the weight of the clay.

Preferably the weight ratio between the ethylenically unsaturated monomer added in step B) and the clay of step A) which is at least partially intercalated with a compound of formula I or II is from 500:1 to 1:5.

In a specific embodiment of the invention the process is carried out wherein a further cationic compound selected from the group of cationic surfactants is added in step A).

Typical surfactants are amino acids or alkylammonium ions.

The amino acid surfactants transfer a proton from the COOH group to the NH₂ group forming a NH₃⁺ group which can exchange with a cation of the clay mineral.

For example the alkylammonium ion is CH₃-(CH₂)_n-NH₃⁺ where n is from 1 to 18. It is believed that the alkylammonium cations readily exchange with the naturally occurring cations present in between the clay platelets resulting in an intercalated state.

It is also possible to repeat the process step B) with a second ethylenically unsaturated monomer which is different from the first one, leading to a block copolymer.

The clay may be a natural or synthetic clay material.

When the clay material is a synthetic one, it may be produced by gas-phase or sol-gel processes, for example SiO_2 , [e.g. Aerosil[®] from Degussa; Ludox[®] from DuPont; Snowtex[®] from Nissan Chemical; Levasil[®] from Bayer; or Sylsia[®] from Fuji Silysia Chemical]; colloidal silica [e.g. Klebosol[®]], or organosols [e.g. Highlink[®] OG from Clariant].

Typical clays are natural or synthetic phyllosilicates, which may be organophilically modified montmorillonites [e.g. Nanomer[®] from Nanocor or Nanofil[®] from Suedchemie], bentonites [e.g. Cloisite[®] from Southern Clay Products], beidellites, hectorites, saponites, nontronites, sauconites, vermiculites, ledikites, magadiites, kenyaite or stevensites.

These materials are commercially available in its natural or partially intercalated form.

Special preference is given to a process wherein the natural or synthetic clay is selected from the group consisting of smectite, phyllosilicate, montmorillonite, saponite, beidellite, nontronite, hectorite, stevensite, vermiculite, kaolinite, hallosite, synthetic phyllosilicates, and combinations thereof.

Most preferred is montmorillonite.

Further aspects of the invention are a monomer/polymer clay nanocomposite dispersion obtainable by a process as described above, a composition comprising an aqueous dispersion of a natural or synthetic clay which is partially intercalated and/or exfoliated and a compound as described above and a composition, which contains additionally an ethylenically unsaturated monomer and/or an organic solvent.

Yet another aspect of the invention is the use of a compound of formula I or II for the polymerization of ethylenically unsaturated monomers and the use of a monomer/polymer clay nanocomposite dispersion obtainable according to the process as defined above as additive in paints, coatings, inks, adhesives, reactive diluents or in thermoplastic materials.

The following examples illustrate the invention.

A) Preparation Examples of the Compounds

Example A1: {4-[1-(4-tert-butyl-2,2-diethyl-6,6-dimethyl-3-oxo-piperazine-1-yloxy)-ethyl]-benzyl}-triethyl-ammonium chloride (compound 101, Table 1)

a) 1-tert-butyl-4-[1-(4-chloromethyl-phenyl)-ethoxy]-3,3-diethyl-5,5-dimethyl-piperazine-2-one

To a solution of 13.4 g (0.052 mol) 1-tert-butyl-3,3-diethyl-5,5-dimethyl-piperazine-2-one-4-N-oxyl (prepared according to Ger. Offen. DE 19949352 A1) and 8 g (0.052 mol) 4-chloromethylstyrene in 320 ml ethanol 5 g (0.00788 mol) (S,S)-Jacobsen catalyst are added. Thereafter 9.6 ml (0.052 mol) t-butylhydroperoxide (70% in H₂O) are added followed by 4 g (0.010 mol) sodiumborohydride. The mixture is stirred at room temperature under argon for 20h and subsequently evaporated under vacuum. The residue is diluted with 50 ml water and then extracted with 2x50 ml dichlormethane. The extract is dried over MgSO₄ and purified by chromatography on silica gel (hexane-ethylacetate 12:1). After crystallisation of the pure fraction from pentane 4.5 g of the title compound are obtained, mp. 66-68 °C.

C₂₃H₃₇ClN₂O₂ (409.02) calculated: C: 67.54%, H 9.12%, N 6.85; found: C 67.58 %, H 9.16%, N 6.77%.

b) Quaternisation

To a solution of 20 ml triethylamine in 20 ml acetonitrile 4 g (0.0098 mol) of the product obtained under a) are added. The solution is stirred for 10 h at 60 °C and evaporated. The solid residue is suspended in 30 ml t-butyl-methyl-ether, filtrated and dried. 4.7 g of the title compound are obtained as a white powder.

¹H-NMR (300 MHz, CDCl₃): 7.57-7.49 m (2ArH), 7.41-7.38 m (2 ArH), 4.93-4.69 m (3H), 3.57-3.37 m (6 H), 3.21-2.93 m (2H), 2.0-0.62 m (37 H).

Example A2: 4-{4-[1-(4-tert-butyl-2,2-diethyl-6,6-dimethyl-3-oxo-piperazine-1-yloxy)-ethyl]-benzoyl}-1,1-dimethyl-piperazine-1-ium iodide (compound 102, Table 1)

a) 1-tert-butyl-3,3-diethyl-5,5-dimethyl-4-[1-[4-(4-methyl-piperazine-1-carbonyl)-phenyl]-ethoxy]-piperazine-2-one

To a solution of 0.5 g (0.00124 mol) 4-[1-(4-tert.-butyl-2,2-diethyl-6,6-dimethyl-3-oxo-piperazin-1-yloxy)-ethyl]-benzoic acid (prepared according to WO 01/02345 A2) in 10 ml dichlormethane 0.4 g (0.00248 mol) carbonyldiimidazol are added. The mixture is stirred for 30 minutes under argon at room temperature. Subsequently 0.275 ml (0.00248 mol) N-methylpiperazine is added and the solution is stirred for further 12 h. The solution is then washed 3 x with 5 ml water, dried over MgSO_4 , and evaporated. The residue is purified by chromatography on silica gel (hexane-ethylacetate 2:1) and 0.46 g of the title compound are obtained as viscous oil.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.39-7.28 m (4 ArH), 4.75-4.69 m (1H), 4-0.65 m (41H).

b) Quaternisation

To a solution of 1 g (0.002 mol) of the product obtained under a) in 2 ml acetonitrile 2 ml methyl iodide are added and the solution is stirred at room temperature for 1 h. After evaporation 1.2 g of the title compound are obtained as yellow powder.

$^1\text{H-NMR}$ (300 MHz, DMSO-d_6): 7.45 s (4 ArH), 4.79-4.73 m (1H), 4.1-0.58 m (43H).

Example A3: {3-[2-(2,6-diethyl-2,3,6-trimethyl-piperidine-1-yloxy)-propionylamino]-propyl}-ethyl-dimethyl-ammonium bromide (compound 103, Table 1)

a) 2-chloro-N-(3-dimethylamino-propyl)-propionamide

To 12.25 g (0.1 mol) 2-chloropropionic acid-methylester 10.25 g (0.1 mol) 3-dimethylamino-1-propylamine are added at such a rate, that the reaction temperature remains below 40 °C. The mixture is stirred for 4 h at room temperature and subsequently evaporated at 40 °C/1 mbar. Thereafter, the methanol formed in the reaction is distilled off. 18.4 g of the title compound are obtained as colorless oil.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.47 bs (NH), 4.41-4.34 q (1H), 3.40-3.34 m (2H), 2.47-2.40 m (2H), 2.24 s (6H), 1.70-1.68 d (3H), 1.73-1.64 m (2H)

b) 2-(2,6-diethyl-2,3,6-trimethyl-piperidine-1-yloxy)-N-(3-dimethylamino-propyl)-propionamide

To a solution of 13.85 g (0.07 mol) 2,6-Diethyl-2,3,6-trimethyl-piperidin-1-N-oxyl (prepared according to Ger. Offen. DE 2621841) in 70 ml ethylacetate 13.9 g (0.14 mol) Cu(I)-chloride are added under argon followed by 24.25 g (0.14 mol) pentamethyldiethylenetriamine (PMDETA). Subsequently within 10 minutes 14.95 g (0.0735 mol) of the product obtained under a) are added dropwise. The mixture is stirred at room temperature for 12h, followed by further addition of 3.05 g of the chloramide prepared under a), 2 g CuCl and 4.3 ml PMDETA, 20 ml ethylacetate and 10 ml DMF. The mixture is then stirred for further 96 h at room temperature. The suspension is filtered and the filter cake is washed with 100 ml

ethylacetate. The filtrate is washed with 3 x 100 ml water, then with 2x60 ml of a 1% aqueous EDTA-disodiumsalt-solution and dried over MgSO_4 . The residue is purified by chromatography on silica gel (hexane-ethylacetate 2:1). 7.7 g of the title compound are obtained as thick yellow oil

$\text{C}_{20}\text{H}_{41}\text{N}_3\text{O}_2$ (355.8) found: $\text{MH}^+ = 356.3$ (APCI-MS).

c) Quaternisation

To a solution of 7.6 g (0.0214 mol) of the product obtained under b) in 10 ml acetonitrile 10 ml ethylbromide are added and the solution is stirred for 12 h at room temperature. After evaporation 9 g of the title compound are obtained as white powder.

For $[\text{C}_{22}\text{H}_{46}\text{N}_3\text{O}_2]^+ \times \text{Br}^- = [384.64] \times [79.904]$; found M^+ (Cation) = 384.6 (Infusion ESI-MS)

Example A4: {3-[2-(2,6-diethyl-4-hydroxy-2,3,6-trimethyl-piperidine-1-yloxy)-propionylamino]-propyl}-ethyl-dimethyl-ammonium bromide (compound 104, Table 1)

a) 2-(2,6-diethyl-4-hydroxy-2,3,6-trimethyl-piperidine-1-yloxy)-N-(3-dimethylamino-propyl)-propionamide

To a solution of 21.4 g (0.1 mol) 2,6-diethyl-4-hydroxy-2,3,6-trimethyl-piperidine-1-N-oxyl (prepared according to Ger. Offen. DE 19909767 A1) in 50 ml DMF 19.8 g (0.2 mol) Cu(I)-chloride are added under argon. Subsequently 34.7 g (0.2 mol) pentamethyldiethylenetriamine (PMDETA) and 22.1 g (0.11 mol) 2-chloro-N-(3-dimethylamino-propyl)-propionamide (prepared according to example A3) are added within 20 minutes. The temperature during addition is kept below 40 °C. The mixture is stirred 4 h at room temperature followed by the addition of 500 ml water and 150 ml dichlormethane. The organic phase is separated and the water phase is extracted with 2x100 ml dichlormethane. The organic phases are washed with 5x100 ml water, then with 3x60 ml 1% aqueous EDTA-Disodiumsalt-solution, dried over MgSO_4 evaporated. 33.55 g of the title compound are obtained as thick yellow oil.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.34-7.14 bs (1H), 4.29-4.20 m (2H), 3.6-3.1 m (2H), 2.6-0.83 m (30H), 2.22 s (6 H).

b) Quaternisation

To a solution of 28.35 g (0.076 mol) of the product obtained under a) in 25 ml acetonitrile 25 ml ethylbromide are added and the solution is stirred for 12 h at room temperature. After evaporation 36.5 g of the title compound are obtained as white powder.

For $[\text{C}_{22}\text{H}_{46}\text{N}_3\text{O}_3]^+ \times \text{Br}^- = [400.626] \times [79.904]$; found M^+ (Kation) = 400.4 (Infusion ESI-MS)

Example A5: [3-(2-{N-.tert.-butyl-.N.-[1-(diethoxy-phosphoryl)-2,2-dimethyl-propyl]-aminoxy}-propionylamino)-propyl]-ethyl-dimethyl-ammonium bromide (compound 105, Table 1)

a) (1-{.tert.-butyl-[1-(3-dimethylamino-propylcarbamoyl)-ethoxy]-amino}-2,2-dimethyl-propyl)-phosphonic acid diethyl ester

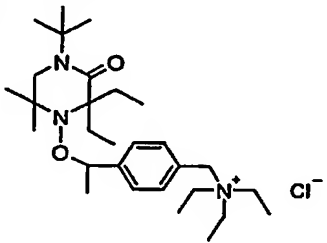
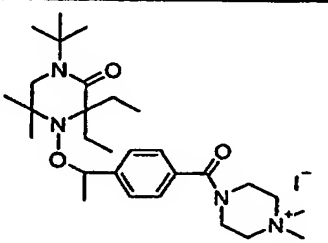
From 5.01 g (0.017 mol) N-(1,1-Dimethylethyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxy (prepared according to Macromolecules (2000), 33(4), 1141-1147), 3.35 g (0.034 mol) CuCl, 5.9 g (0.034 mol) PMDETA and 3.95 g (0.0196 mol) 2-chloro-N-(3-dimethylamino-propyl)-propionamide (prepared according to example A3) in 10 ml DMF 5.6g of the title compound are obtained as thick yellowish oil in analogy to example A4 (reaction time 19 h). For $C_{21}H_{46}N_3O_5P$ (451.59) calculated C 55.85%, H 10.27%, N 9.31%; found C 55.09%, H 9.91%, N 8.86%.

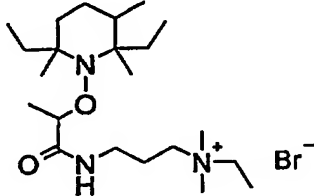
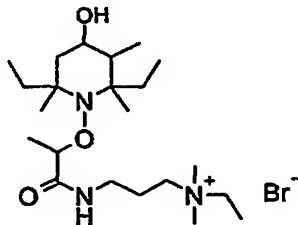
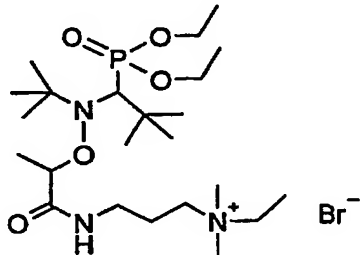
b) Quaternisation

To a solution of 4.95 g (0.011 mol) of the product obtained under a) in 23 ml acetonitrile 3.3 ml ethylbromide are added and the solution is stirred for 17 h at room temperature. The suspension is evaporated, the residue is suspended in 25 ml diethylether and filtered. 5.45 g of the title compound are obtained as a white powder.

The compounds are summarized in Table 1

Table 1

No	Structure	No.	Structure
101		102	

103		104	
105			

B) Application Examples

Polymerization of n-butyl acrylate with cationic alkoxyamines (NOR's)

The cationic NOR's are tested in pure n-butyl acrylate monomer: In a 50 ml round bottom flask with vacuum and nitrogen inlet and magnetic stirrer 10 g n-butyl acrylate (BASF, techn. quality) is mixed with 1.5 mol% of the cationic alkoxyamine (NOR), evacuated and purged with nitrogen 3 times and polymerized at 140°C on an oil bath for 7-20 h under good stirring. The conversion is measured by ¹H-NMR, M_n and PDI with GPC in THF, values are relative to PS-standards.

Table 2

NOR	Zeit	Umsatz % (¹ H-NMR)	M _n (gef.)	PDI
Example B1 Compound 101	17 h	90 %	6980	1.47
Example B2 Compound 102	20 h	78 %	5470	1.24
Example B3 Compound 103	7 h	70 %	6660	1.68
Example B4 Compound 104	7 h	60 %	5080	1.46

The results presented in Table 1 clearly show that all compounds are able to initiate a controlled polymerization of n-butylacrylate.

Ex 6-8: Intercalation of sheet silicates with cationic NOR's

Ex. 6: Intercalation of Nanofil EXM 588 (Layered silicate of Montmorillonite-type from Süd Chemie, Germany) with compound 101.

In a 50 ml round bottom flask 2.0 g Nanofil EXM 588 is dispersed in 30 ml of a 0.05 M solution of compound 101 in water and stirred with magnetic stirring during 24 h at R.T. After centrifugation (IEC Centra GP8 Zentrifuge, 100-180 ml glass vessels) with 2000 rpm (corresponding to ca. 850 g) during 20 min, a sample is taken of the supernatant clear solution, from which the concentration of remaining (= non intercalated) compound 101 is determined by UV-spektroskopy at $\lambda=245$ nm. The intercalated quantity of compound 101 is determined to be 358 mg (=0.702 mmol) for 1 g of layered silicate.

The supernatant solution is decanted and the solid washed with water, centrifugation and decantation 3 times. This procedure is repeated with MeOH. The sedimented, washed product is subjected to a powder X-ray ($\lambda=1.54$ Angström), giving a main reflection at $2\Theta_{\max}=3.86^\circ$, which corresponds to an interlayer distance d of 2.29 nm. Compared with the native sheet silicate ($2\Theta_{\max}=7.1^\circ$, $\Rightarrow d=1.24$ nm) an increase of the interlayer distance of 1.05 nm is obtained, corresponding to approximately the size of the intercalated molecule. The reflex at $2\Theta_{\max}=7.1^\circ$ ($d=1.24$ nm), corresponding to the original sheet distance has almost completely disappeared.

In order to check the adsorbed quantity of intercalated CG42-0194, a sample is completely dried in vacuum and their weight loss determined by thermogravimetric analysis (TGA): heating rate: $10^\circ\text{C}/\text{min}$, from room temperature to 600°C . The obtained weight loss of 26.3% corresponds very well to the theoretical value of 26.4%.

Ex. 7-8: In analogy to Ex. 6, the following cationic NOR's are intercalated into Nanofil EXM 588: The results are given in Table 3.

Table 3

Example No.	NOR	Interkalierte Menge an NOR*	Schichtabstand nach Interkalation	Bemerkungen
Example B7	Compound 104	22.7 wt.% (=0.47 mmol/g)	$2\Theta_{\max}=4.2^\circ$, $\Rightarrow d=2.11 \text{ nm}$	\approx complete exchange
Example B8	Compound 103	24.9 wt.% (=0.53 mmol/g)	$2\Theta_{\max}=4.3^\circ$, $\Rightarrow d=2.03 \text{ nm}$	\approx complete exchange

*based on the total weight layered silicate + NOR compound

Ex. 9: Polymerizations

Ex. 9: In a 50 ml round bottom flask with magnetic stirring and vacuum and nitrogen inlet 0.5 g with compound 101 intercalated Nanofil EXM588 in 9.5 g n-butyl acrylate (BASF, techn. quality) and 4.28 g 2-methoxypropyl acetat is dispersed and homogenized in an ultrasonic bath. After evacuation and purging 5 times with N_2 , the monomer is polymerized during 9 h at 140°C (bath temperature) under vigorous stirring. The monomer conversion, determined by $^1\text{H-NMR}$, is 85%. The dispersion is subjected to centrifugation at 2000 rpm during 60 min and the sedimented solid washed with EtOAc and dried. 57 mg are obtained. It is shown using TGA (see ex. 6: weight loss 25° to 600°C : 26%, theory: 23%) that the solid is pure intercalated Nanofil EXM 588 with compound 101 and does not contain polymer.

The supernatant solution is evaporated and dried. According to TGA analysis the composition contains approximately 10% layered silicate and 90% polymer.

The X-ray analysis of the solid gave only peaks at $2\Theta > 10^\circ$, which indicates complete exfoliation. A sample (150 mg) of this solid is refluxed with 15 ml 0.1 M LiBr solution in THF during 17 h at 65°C , to cleave off the polymer from the sheet silicate. After filtration molar mass (M_n) and PDI is determined by GPC in THF (relative to PS-standards): $M_n=18000$, $M_w=38600$, $\text{PDI}=2.15$.

The supernatant solution can be centrifuged during many hours (2000 rpm, corresponding to ca. 850 g), without further sedimentation. Even after 10-fold dilution with EtOAC it is stable

for months (no sedimentation observed) which proves the nm size of the particles, indicating complete exfoliation.

Comparative Example 10.

The experiment is performed in analogy to example 9 using 0.5 g with α,α' -azodiisobutyramidine-dihydrochloride intercalated Nanofil EXM588 in 9.5 g n-butyl acrylate, without further solvent. Polymerization: 3 h at 80°C (bath temperature).

The dispersion is diluted with 240 ml toluene and 20 min centrifuged at 2000 rpm. After washing and drying 0.35 g of a solid is obtained which corresponds according to TGA analysis to pure with α,α' -azodiisobutyramidine-dihydrochloride intercalated Nanofil EXM588 and contains no polymer!

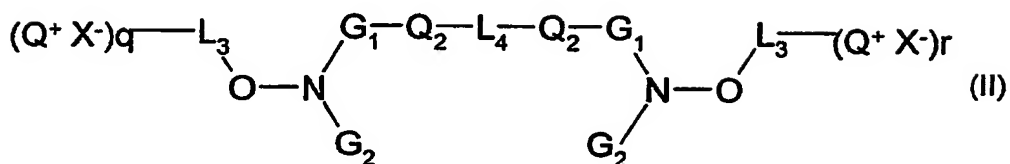
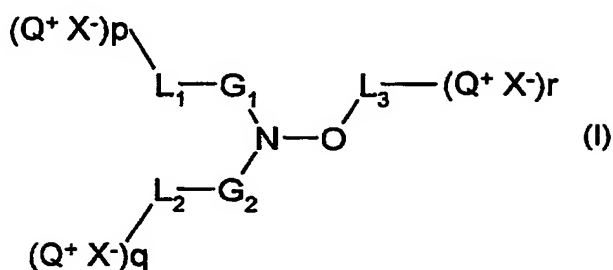
The supernatant solution is completely evaporated and the residue dissolved in 150 ml THF. Centrifugation 1 h with 2000 rpm gives again 50 mg with α,α' -azodiisobutyramidine-dihydrochloride intercalated Nanofil EXM588. After evaporation of all solvent and drying 24 h at 60°C in vacuum 2.0 g polymer with ca. 0.1 g with α,α' -azodiisobutyramidine-dihydrochloride intercalated Nanofil EXM5881 is obtained in accordance with the TGA analysis: Weight loss 25° to 600°C: 97% (calculated: 96.5%).

A sample (150 mg) of this solid is refluxed with 15 ml 0.1 M LiBr solution in THF during 17 h at 65°C in order to separate the polymer from the sheet silicate. Afterwards the solution is filtered and M_n and PDI determined by GPC in THF (relative to PS-standards): $M_n=658000$, $M_w=1360000$, PDI=2.06.

The comparison of inventive example 9 with comparative example 10 shows that the exfoliation of the layered silicate using intercalated NOR (ex. 9) followed by controlled radical polymerization is much more efficient: Firstly a much higher monomer conversion (85% compared to 20%) is obtained; secondly only a small amount of the layered silicate is not exfoliated (11.4% compared with 80% in ex. 10), which can be explained by an efficient initiation in all layers, and thirdly the formed polymer has a much lower, controlled molecular weight.

Claims

1. A compound of formula (I) or (II)



wherein

G₁ and G₂ independently represent a tertiary carbon atom to which unsubstituted C₁-C₁₈alkyl or phenyl or with CN, COC₁-C₁₈alkyl, CO-phenyl, COOC₁-C₁₈alkyl, OC₁-C₁₈alkyl, NO₂, NHC₁-C₁₈alkyl or N(C₁-C₁₈)₂alkyl substituted alkyl or phenyl groups are bonded; or one of

G₁ and G₂ is a secondary carbon atom to which a group -P(O)(OR₂₂)₂ and the other is as defined above; or

G₁ and G₂ together with the nitrogen atom to which they are bonded form a 5 to 8 membered heterocyclic ring or a polycyclic or spirocyclic 5 to 20 membered heterocyclic ring system, which is substituted with 4 C₁-C₄alkyl groups or 2 C₅-C₁₂ spirocycloalkyl groups in ortho position to the nitrogen atom and which may be further substituted with one or more C₁-C₁₈alkyl, C₁-C₁₈alkoxy or =O groups; and

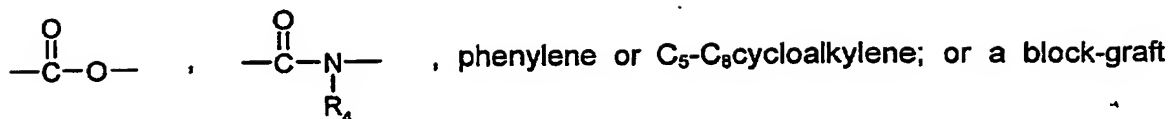
which may be interrupted by a further oxygen or nitrogen atom;

with the proviso that at least one of the 4 C₁-C₄alkyl groups in ortho position to the nitrogen atom is higher alkyl than methyl;

L₁, L₂ and L₄ is a linking group selected from the group consisting of

a direct bond, R₁-Y or R₂-C(O)-Y- where Y is attached to G₁ and/or G₂; C₁-C₂₅alkylene,

C₂-C₂₅alkylene interrupted by -O-, -S-, -SO-, -SO₂-, >N-R_3 , $\text{--}\overset{\text{O}}{\parallel}\text{C--}$,



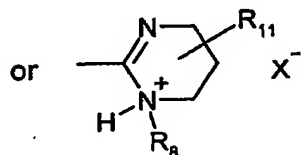
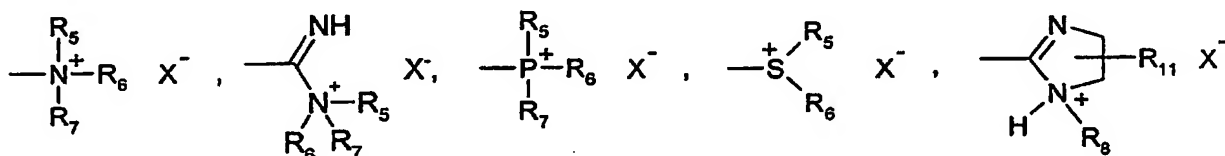
copolymer,

Y is O, or NR_9

L_3 is a group containing at least one carbon atom and is such that the radical $\bullet\text{L}_3\text{-(Q}^+\text{X}^-)$ derived from the group is able to initiate polymerization of ethylenically unsaturated monomers;

Q_2 is a direct bond, O, NR_5 or NR_5R_6 ;

Q^+ is a cationic group selected from the group consisting of



wherein

R_1 is $\text{C}_1\text{-C}_{18}$ alkylene,

R_2 is a direct bond or $\text{C}_1\text{-C}_{18}$ alkylene,

R_3 is hydrogen or $\text{C}_1\text{-C}_8$ alkyl,

R_4 is hydrogen or $\text{C}_1\text{-C}_4$ alkyl,

R_5 , R_6 and R_7 are each independently of the others hydrogen, $\text{C}_1\text{-C}_{18}$ alkyl,

$\text{C}_3\text{-C}_{12}$ cycloalkyl, phenyl or $\text{C}_7\text{-C}_9$ phenylalkyl or $\text{C}_6\text{-C}_{10}$ heteroaryl which all may be unsubstituted or substituted by halogen, OH, NO_2 , CN, $\text{C}_1\text{-C}_4$ alkoxy, or

R_5 , R_6 and R_7 together with the nitrogen to which they are bonded form a 3-12 membered monocyclic or polycyclic ring which may contain further heteroatoms;

R_8 is hydrogen or $\text{C}_1\text{-C}_{25}$ alkyl, $\text{C}_3\text{-C}_{25}$ alkyl interrupted by oxygen, sulfur or by



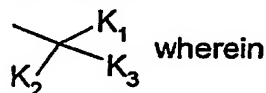
R_9 is hydrogen, C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl, C_3 - C_{18} alkinyl, phenyl, C_7 - C_9 phenylalkyl, which all may be unsubstituted or substituted by one or more hydroxy, halogen or C_1 - C_4 alkoxy groups;

R_{11} is hydrogen or C_1 - C_{18} alkyl;

R_{22} is C_1 - C_{18} alkyl;

X^- is the anion of a C_1 - C_{18} carboxylic acid which may contain more than one carboxylic acid group, fluoride, chloride, bromide, iodide, nitrite, nitrate, hydroxide, acetate, hydrogen sulfate, sulfate, C_1 - C_{18} alkoxy sulfate, aromatic or aliphatic sulfonate, carbonate, hydrogen carbonate, perchlorate, chlorate, tetrafluoroborate, borate, phosphate, hydrogenphosphate, dihydrogenphosphate or mixtures thereof; and
p, q, and r are independently of each other a number from 0 to 10 and at least one is different from 0.

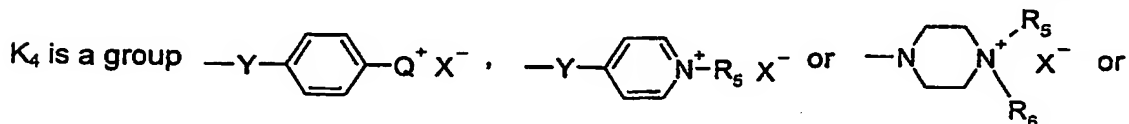
2. A compound according to claim 1 wherein in formula I or II $-L_1(Q^+X^-)$, $-L_2(Q^+X^-)$, and $-L_3(Q^+X^-)$, are a group



K_1 and K_2 are hydrogen, C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl and

K_3 is a group $-COK_4$ or $Z-K_5$ where

K_4 is $-Y-[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6R_7X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-$ or $-Y-CH_2-CHOH-CH_2-N^+R_5R_6R_7X^--[[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6R_7X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-]_u$, where s is a number 0-8, t is a number 0-4 and u is 0 or 1 and Y is $-O-$ or NR_9 ; or

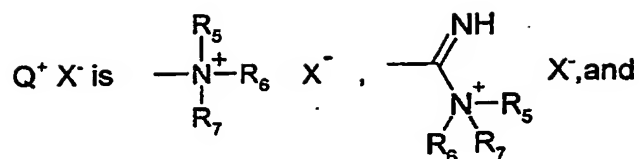


Z is $-C(O)-$ or a direct bond,

if Z is $-C(O)-$, K_5 has the same meaning as K_4 ,

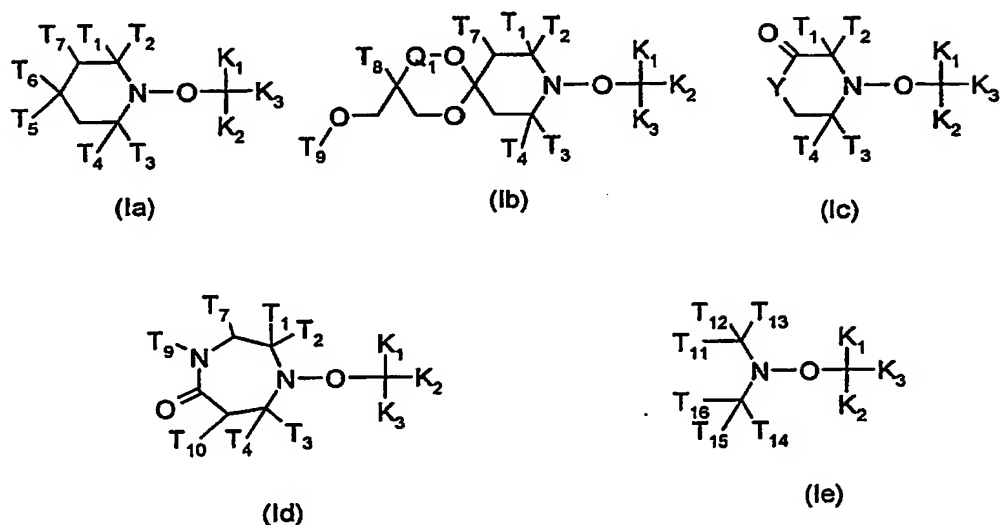
if Z is a direct bond, K_5 is $Y-CH_2-CHOH-CH_2-N^+R_5R_6R_7X^--[[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6R_7X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-]_u$, Q^+X^- , $-CH_2Q^+X^-$ or $-CHCH_3Q^+X^-$;

and Y is $-O-$, $-NR_9$ or a direct bond;



the other substituents are as defined in claim 1.

3. A compound according to claim 1 of formulae Ia, Ib, Ic, Id or Ie



wherein

Q₁ is a direct bond or a -CH₂- group;

if Q₁ is a direct bond, T₈ is hydrogen,

if Q₁ is -CH₂-, T₈ is methyl or ethyl;

T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;

T₇ and T₁₀ are independently hydrogen or methyl;

T₅ and T₆ are hydrogen or

T₅ and T₆ together are a group =O, =NOH, =NO-T₉ or

T₅ is hydrogen and T₆ is -O-T₉ or -NR₉-T₉ where T₉ is hydrogen, R₉ or -C(O)-R₉, where R₉ is hydrogen, C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkinyl, phenyl, C₇-C₉phenylalkyl, which may be unsubstituted or substituted by one or more hydroxy, halogen or C₁-C₄alkoxy groups;

T₁₁, T₁₂, T₁₃, T₁₄, T₁₅ and T₁₆ independently are C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkinyl, C₅-C₁₂cycloalkyl, phenyl or C₇-C₉phenylalkyl; or

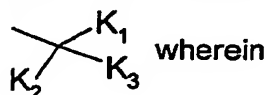
T_{11} is hydrogen and T_{12} is a group $-P(O)(OC_2H_5)_2$ and the others are as defined above;

or T_{11} and T_{14} are a group $-CH_2-O-T_9$ and the others are as defined above; or

T_{16} is a group $-C(O)-Y-R_5$ and the others are as defined above; or

T_{11} , T_{12} and T_{13} are a group $-CH_2OH$;

$-L_3(Q^+X^-)$, is a group



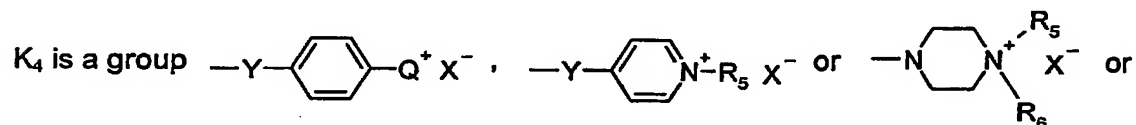
K_1 and K_2 are hydrogen, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl and

K_3 is a group $-COK_4$ or $-\text{C}_6\text{H}_4-Z-K_5$ where

K_4 is $Y-[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-$ or

$-Y-CH_2-CHOH-CH_2-N^+R_5R_6X^- - \{[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-\}_u$,

where s and t is a number 0-4 and u is 0 or 1; or

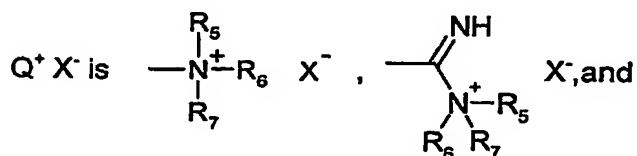


Z is $-C(O)-$ or a direct bond,

if Z is $-C(O)-$ K_5 has the meaning of K_4 ,

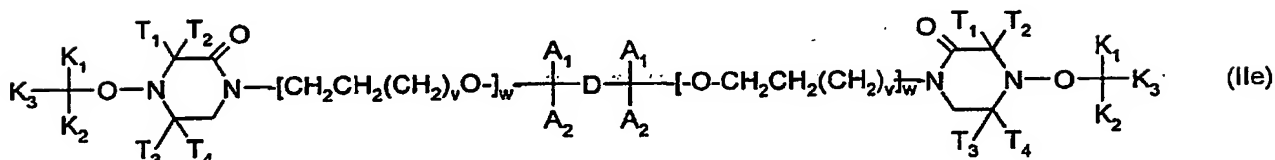
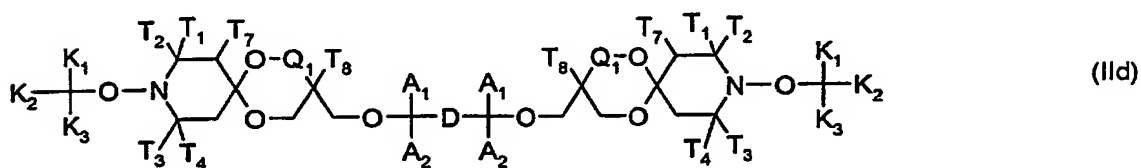
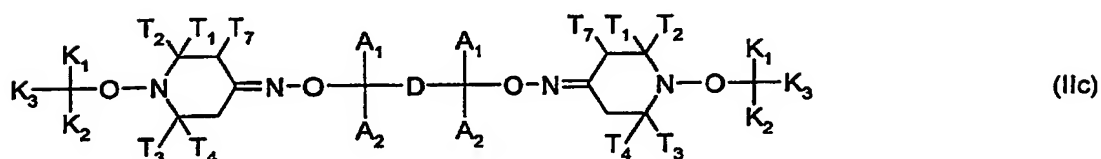
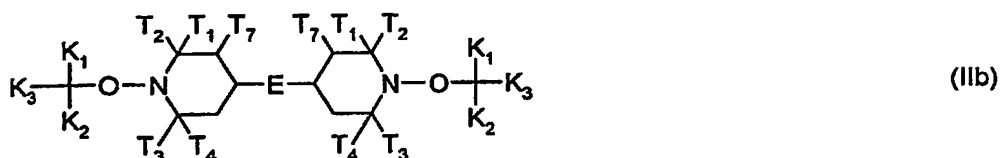
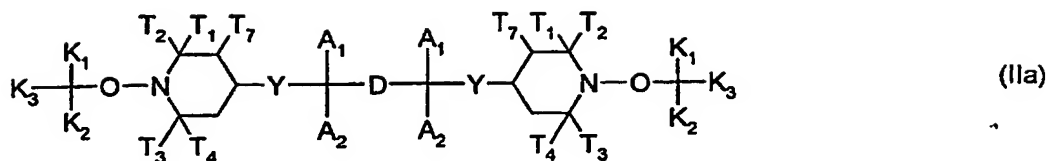
if Z is a direct bond, K_5 is $O-CH_2-CHOH-CH_2-N^+R_5R_6X^- - \{[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-\}_u$, Q^+X^- , $-CH_2Q^+X^-$ or $-CHCH_3Q^+X^-$;

Y is $-O-$ or $-NR_9$;



X^- and the other substituents are as defined in claim 1.

4. A compound according to claim 1 of formula IIa, IIb, IIc, IId or IIe

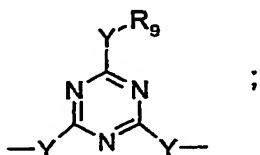


wherein

A_1 and A_2 are independently hydrogen or together with the carbon atom to which they are bonded form a carbonyl group, $-\text{C}(\text{O})-$;

D is a direct bond or C_1 - C_{12} alkylene, C_1 - C_{12} alkylene which is interrupted by one or more O , S , or NR_9 atoms, C_5 - C_{12} cycloalkylene or phenylene;

E is a group $-\text{NR}_9-(\text{CH}_2)_x-\text{NR}_9-$ where x is a number from 2 to 12 or a group



v is a number from 0 to 10 and w is 0 or 1;

Q_1 is a direct bond or a $-CH_2-$ group;

if Q_1 is a direct bond, T_8 is hydrogen,

if Q_1 is $-CH_2-$, T_8 is hydrogen, methyl or ethyl;

Y is $-O-$ or $-NR_9$;

T_1 , T_2 , T_3 and T_4 are independently methyl or ethyl with the proviso that at least one is ethyl;

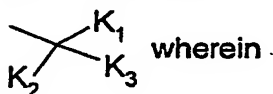
T_7 is hydrogen or methyl;

T_5 and T_6 are hydrogen or

T_5 and T_6 together are a group $=O$, $=NOH$, $=NO-T_9$ or

T_5 is hydrogen and T_6 is $-O-T_9$ or $-NR_9-T_9$ where T_9 is hydrogen, R_9 or $-C(O)-R_9$, where R_9 is hydrogen, C_1-C_{18} alkyl, C_3-C_{18} alkenyl, C_3-C_{18} alkynyl, phenyl, C_7-C_9 phenylalkyl, which may be unsubstituted or substituted by one or more hydroxy, halogen or C_1-C_4 alkoxy groups;

$-L_3(Q^+X^-)$, is a group



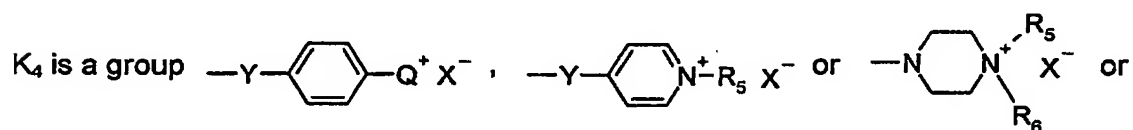
K_1 and K_2 are hydrogen, C_5-C_{12} cycloalkyl, phenyl or C_7-C_9 phenylalkyl and

K_3 is a group $-COK_4$ or $-\text{C}_6\text{H}_4-Z-K_5$ where

K_4 is $Y-[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-$ or

$-Y-CH_2-CHOH-CH_2-N^+R_5R_6X^--[[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-]_u$,

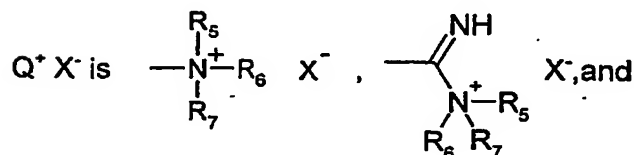
where s and t is a number 0-4 and u is 0 or 1; or



Z is $-C(O)-$ or a direct bond,

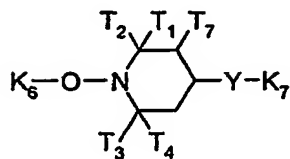
if Z is $-C(O)-$ K_5 has the meaning of K_4 ,

if Z is a direct bond, K_5 is $O-CH_2-CHOH-CH_2-N^+R_5R_6X^--[[(CH_2-CH_2)-(CH_2)_s-N^+R_5R_6X^-]_t-CH_2-CH_2-(CH_2)_s-N^+R_5R_6R_7X^-]_u$, Q^+X^- , $-CH_2Q^+X^-$ or $-CHCH_3Q^+X^-$;

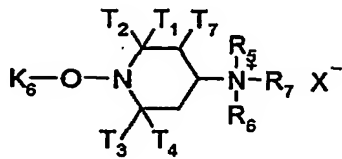


X^- and the other substituents are as defined in claim 1.

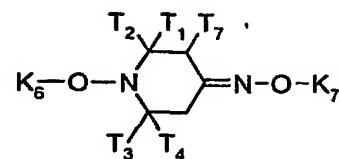
5. A compound according to claim 1 of formula IIIa, IIIb, IIIc, IIId or IIIe



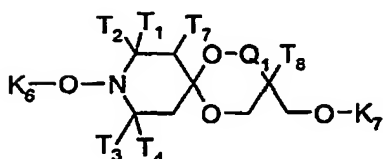
(IIIa)



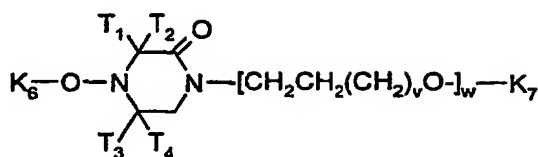
(IIIb)



(IIIc)



(IIIId)



(IIIe)

T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;

T₇ is hydrogen or methyl;

Y is O or NR₉;

Q₁ is a direct bond or a -CH₂- group;

if Q₁ is a direct bond, T₈ is hydrogen,

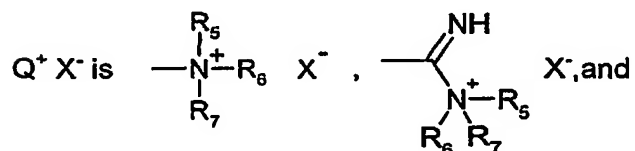
if Q₁ is -CH₂-, T₈ is methyl or ethyl;

v is a number from 0 to 10 and w is 0 or 1;

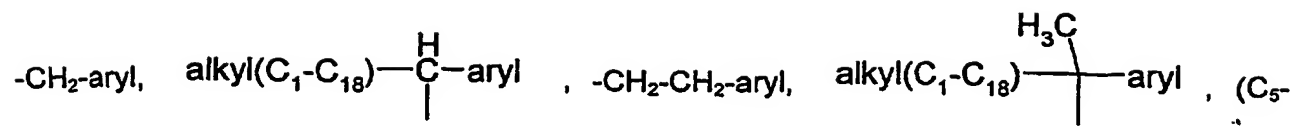
K₇ is a group -CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻ -{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t}-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u,

where s and t is a number 0-4 and u is 0 or 1; or a group -D₁- Q⁺ X⁻ where

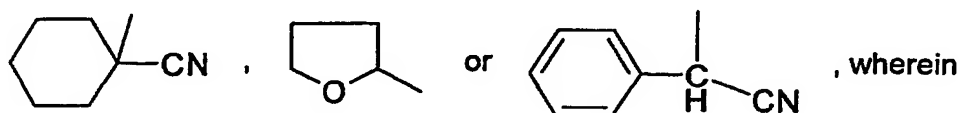
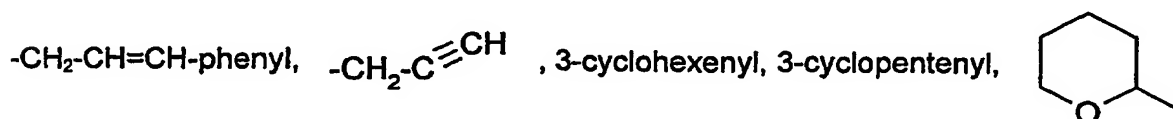
D₁ is C₁-C₁₂alkylene, C₁-C₁₂alkylene which is interrupted by one or more O, S, or NR₉ atoms, C₅-C₁₂cycloalkylene or phenylene;



K₆ is selected from the group consisting of



C₆cycloalkyl)₂CCN, (C₁-C₁₂alkyl)₂CCN, -CH₂CH=CH₂, (C₁-C₁₂)alkyl-CR₃₀-C(O)-(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₃₀-C(O)-(C₆-C₁₀)aryl, (C₁-C₁₂)alkyl-CR₃₀-C(O)-(C₁-C₁₂)alkoxy, (C₁-C₁₂)alkyl-CR₃₀-C(O)-phenoxy, (C₁-C₁₂)alkyl-CR₃₀-C(O)-N-di(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₃₀-CO-NH(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₃₀-CO-NH₂, -CH₂CH=CH-CH₃, -CH₂-C(CH₃)=CH₂,



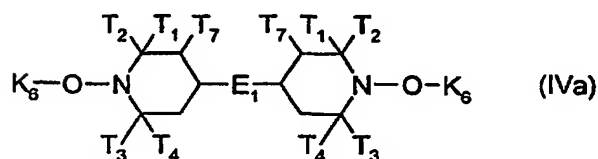
R₃₀ is hydrogen or C₁-C₁₂alkyl;

the alkyl groups are unsubstituted or substituted with one or more -OH, -COOH or -C(O)R₃₀ groups; and

the aryl groups are phenyl or naphthyl which are unsubstituted or substituted with C₁-C₁₂alkyl, halogen, C₁-C₁₂alkoxy, C₁-C₁₂alkylcarbonyl, glycidyloxy, OH, -COOH or -COO(C₁-C₁₂)alkyl and

X⁻ and the other substituents are as defined in claim 1.

6. A compound according to formula IVa



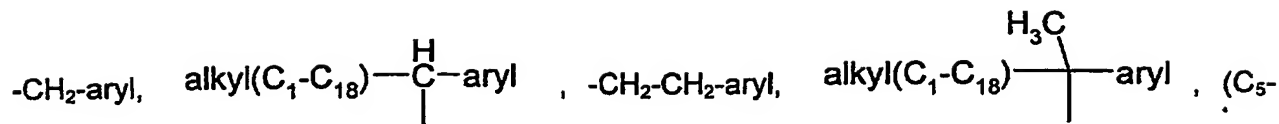
wherein

T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;

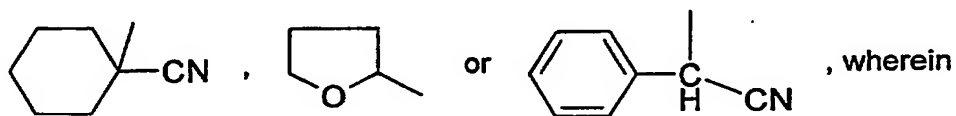
T₇ is hydrogen or methyl;

E₁ is -N⁺ X⁻ R₅R₆-(CH₂)_x-N⁺ X⁻ R₅R₆ where x is a number from 2 to 12;

K₆ is selected from the group consisting of



C₆cycloalkyl)₂CCN, (C₁-C₁₂alkyl)₂CCN, -CH₂CH=CH₂, (C₁-C₁₂)alkyl-CR₃₀-C(O)-(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₃₀-C(O)-(C₆-C₁₀)aryl, (C₁-C₁₂)alkyl-CR₂₀-C(O)-(C₁-C₁₂)alkoxy, (C₁-C₁₂)alkyl-CR₃₀-C(O)-phenoxy, (C₁-C₁₂)alkyl-CR₃₀-C(O)-N-di(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₃₀-CO-NH(C₁-C₁₂)alkyl, (C₁-C₁₂)alkyl-CR₃₀-CO-NH₂, -CH₂CH=CH-CH₃, -CH₂-C(CH₃)=CH₂,



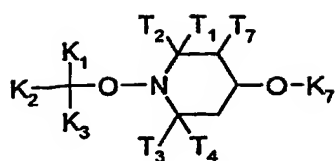
R₃₀ is hydrogen or C₁-C₁₂alkyl;

the alkyl groups are unsubstituted or substituted with one or more -OH, -COOH or -C(O)R₃₀ groups; and

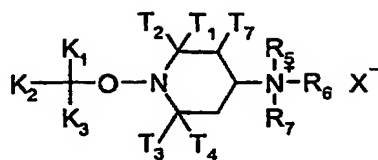
the aryl groups are phenyl or naphthyl which are unsubstituted or substituted with C₁-C₁₂alkyl, halogen, C₁-C₁₂alkoxy, C₁-C₁₂alkylcarbonyl, glycidyloxy, OH, -COOH or -COO(C₁-C₁₂)alkyl and

X⁻ and the other substituents are as defined in claim 1.

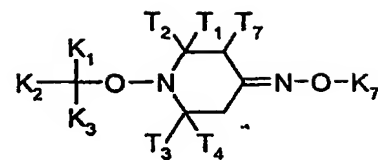
7. A compound according to claim 1 of formula Va, Vb, Vc, Vd or Ve



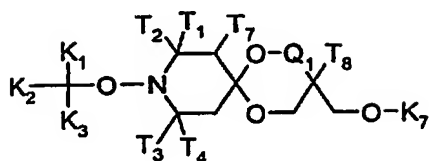
(Va)



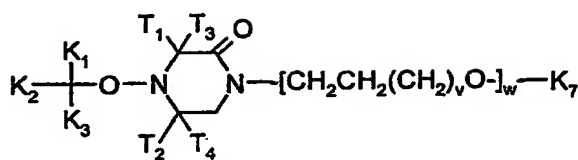
(Vb)



(Vc)



(Vd)



(Ve)

wherein

T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;

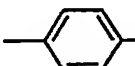
T₇ is hydrogen or methyl;

Q₁ is a direct bond or a -CH₂- group;

if Q₁ is a direct bond, T₈ is hydrogen,

if Q₁ is -CH₂-, T₈ is methyl or ethyl;

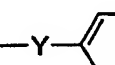
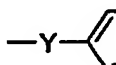
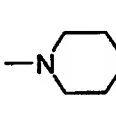
K₁ and K₂ are hydrogen, C₅-C₁₂cycloalkyl, phenyl or C₇-C₉phenylalkyl and

K₃ is a group -COK₄ or  where

K₄ is Y-[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻ or

-Y-CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u,

where s and t is a number 0-4 and u is 0 or 1; or

K₄ is a group  ,  or  or

Z is -C(O)- or a direct bond,

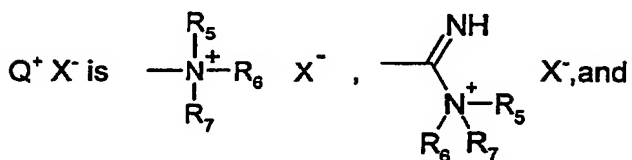
if Z is -C(O)- K₅ has the meaning of K₄,

if Z is a direct bond, K₅ is O-CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u, Q⁺X⁻, -CH₂Q⁺X⁻ or -CHCH₃Q⁺X⁻;

K₇ is a group -CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u ,

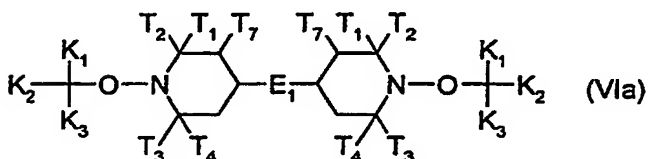
where s and t is a number 0-4 and u is 0 or 1; or a group -D₁- Q⁺ X⁻ where

D₁ is C₁-C₁₂alkylene, C₁-C₁₂alkylene which is interrupted by one or more O, S, or NR₉ atoms, C₅-C₁₂cycloalkylene or phenylene;



X⁻ and the other substituents are as defined in claim 1.

8. A compound according to claim 1 of formula VIa



wherein

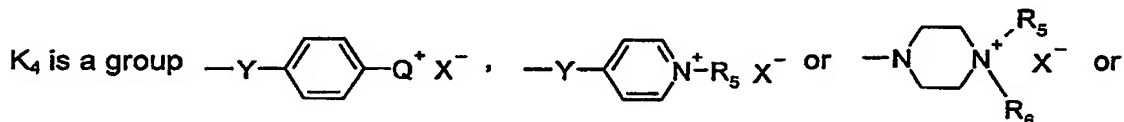
T₁, T₂, T₃ and T₄ are independently methyl or ethyl with the proviso that at least one is ethyl;
T₇ is hydrogen or methyl;

E₁ is -N⁺ X⁻ R₅R₆-(CH₂)_x-N⁺ X⁻ R₅R₆ where x is a number from 2 to 12;

K₁ and K₂ are hydrogen, C₅-C₁₂cycloalkyl, phenyl or C₇-C₉phenylalkyl and

K₃ is a group -COK₄ or $\text{---} \text{C}_6\text{H}_4 \text{---} Z \text{---} K_5$ where

K₄ is Y-[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻ or
-Y-CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u,
where s and t is a number 0-4 and u is 0 or 1; or



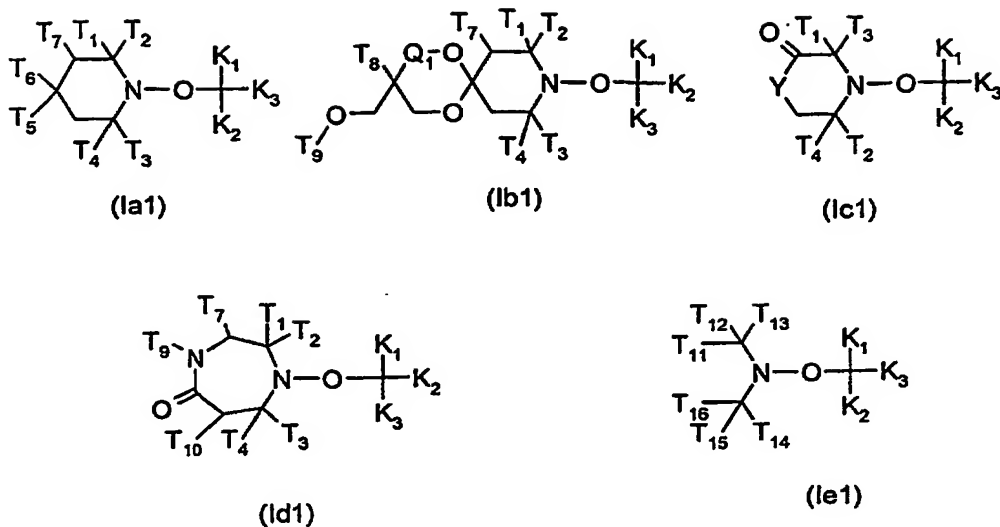
Z is -C(O)- or a direct bond,

if Z is -C(O)- K₅ has the meaning of K₄,

if Z is a direct bond, K₅ is O-CH₂-CHOH-CH₂-N⁺ R₅R₆ X⁻-{[(CH₂-CH₂)-(CH₂)_s-N⁺ R₅R₆ X⁻]_t-CH₂-CH₂-(CH₂)_s-N⁺ R₅R₆R₇ X⁻]_u, Q⁺X⁻, -CH₂Q⁺X⁻ or -CHCH₃Q⁺X⁻ and

X⁻ and the other substituents are as defined in claim 1.

9. A compound according to claim 3 of formula Ia1, Ib1, Ic1, Id1 or Ie1



wherein

Q_1 is a direct bond or CH_2 ;

T_1, T_3 are ethyl and T_2, T_4 and T_7 are methyl;

if Q_1 is a direct bond, T_8 is H;

if Q_1 is CH_2 , T_8 is methyl or ethyl;

T_{10} is H if T_7 is methyl or T_{10} is methyl if T_7 is H;

$T_{11}, T_{12}, T_{13}, T_{14}, T_{15}$ and T_{16} are independently methyl or ethyl; or

T_{11} is H, T_{12} is isopropyl, T_{13} is phenyl and T_{14}, T_{15}, T_{16} are methyl; or

T_{11} is H, T_{12} is $-P(=O)(OC_2H_5)_2$, T_{13} is t-butyl and T_{14}, T_{15}, T_{16} are methyl; or

T_{11} and T_{14} are $-CH_2O-T_9$ and T_{12}, T_{15} are methyl or phenyl and T_{13}, T_{16} are methyl or ethyl;

or

$T_{11}, T_{12}, T_{13}, T_{14}, T_{15}$ are methyl and T_{16} is a group $-CO-O-R_9$ or $-CON(R_9)_2$; or

T_{11}, T_{12} and T_{13} are $-CH_2OH$, T_{14} is H, T_{15} is isopropyl and T_{16} phenyl;

K_1 is H, K_2 is methyl or ethyl and

K_3 is a group $-CO-K_4$ or $-\text{C}_6\text{H}_4-Z-K_5$;

K_4 is $-Y-CH_2-CH_2-(CH_2)_s-N^+X^-R_5R_6R_7$ or;

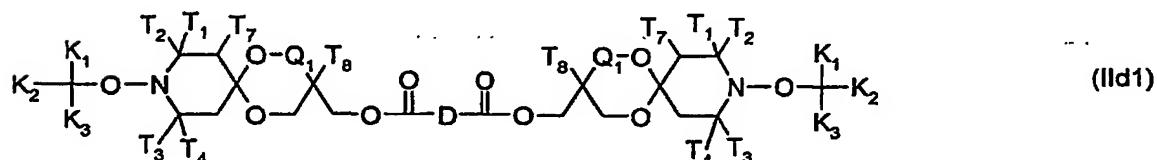
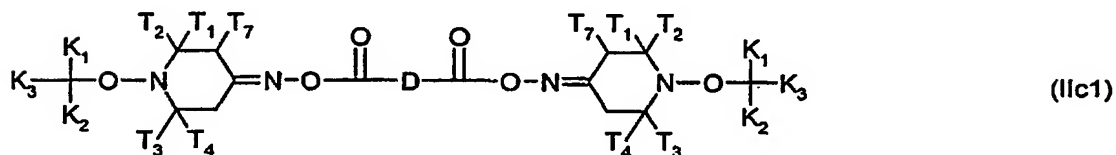
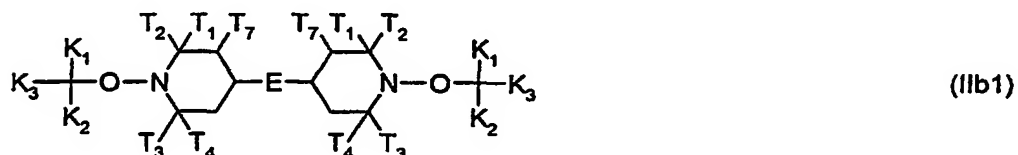
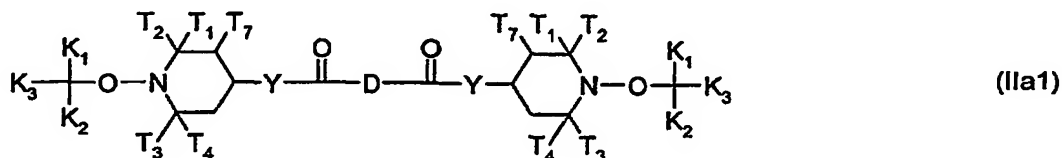
$-Y-CH_2-CHOH-CH_2-N-CH_2-CH_2-(CH_2)_s-N^+X^-R_5R_6R_7$ where Y is O or NR_9 and s is a number from 0 to 2;

if K_3 is $-\text{C}_6\text{H}_4-Z-K_5$, Z is $-CO-$ or a direct bond;

if Z is $-CO-$, K_5 has the same meaning as K_4 ;

if Z is a direct bond, K_5 is a group $-O-CH_2-CHOH-CH_2-N-CH_2-CH_2-(CH_2)_s-N^+X^-R_5R_6R_7$ or $-CH_2N^+R_5R_6R_7 X^-$ and X^- and the other substituents are as defined in claim 1.

10. A compound according to claim 4 of formula IIa1, IIb1, IIc1 or II d1



wherein

Q_1 is a direct bond or CH_2 ;

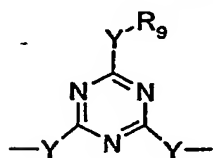
T_1, T_3 are ethyl and T_2, T_4 and T_7 are methyl;

if Q_1 is a direct bond, T_8 is H;

if Q_1 is CH_2 , T_8 is methyl or ethyl;

D is a direct bond, C_1 - C_{12} alkylene or phenylene;

E is $-NR_5-(CH_2)_x-NR_5-$ where x is 2 to 12 or a group



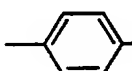
wherein Y is $=NR_9$

K_1 is H, K_2 is methyl or ethyl and

K_3 is a group $-\text{CO}-K_4$ or  $-\text{Z}-K_5$;

K_4 is $-\text{Y}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_s-\text{N}^+\text{X}^-\text{R}_5\text{R}_6\text{R}_7$ or;

$-\text{Y}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_s-\text{N}^+\text{X}^-\text{R}_5\text{R}_6\text{R}_7$ where Y is O or NR_9 and s is a number from 0 to 2;

if K_3 is  $-\text{Z}-K_5$, Z is $-\text{CO}-$ or a direct bond;

if Z is $-\text{CO}-$ K_5 has the same meaning as K_4 ;

if Z is a direct bond K_5 is a group $-\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_s-\text{N}^+\text{X}^-\text{R}_5\text{R}_6\text{R}_7$
or $-\text{CH}_2\text{N}^+\text{R}_5\text{R}_6\text{R}_7 \text{X}^-$;

and

X^- and the other substituents are as defined in claim 1.

11. A process for preparing a monomer/polymer clay nanocomposite dispersion comprising the steps of

- A) providing a first aqueous dispersion of a natural or synthetic clay which can be partially intercalated and/or exfoliated and wherein said clay has an exchangeable cation;
adding a compound according to claim 1 to said dispersion and exchanging said cation at least partially;
- B) adding to said dispersion at least one ethylenically unsaturated monomer and polymerizing at least a portion of said ethylenically unsaturated monomer.

12. A process according to claim 11 wherein the water phase of step A) is at least partially removed before performing step B).

13. A process according to claim 11 wherein in step B) an organic solvent is additionally added.

14. A process according to claim 11 wherein the polymerization is carried out by applying heat, at a temperature of from 60° C to 160° C.

15. A process according to claim 11 wherein the compound according to claim 1 is added in an amount of from 1% to 100% by weight, based on the weight of the clay.

16. A process according to claim 11 wherein the weight ratio between the ethylenically unsaturated monomer added in step B) and the clay of step A) which is at least partially intercalated with a compound according to claim 1 is from 500:1 to 1:5.

17. A process according to claim 11 wherein the ethylenically unsaturated monomer or oligomer is selected from the group consisting of styrene, substituted styrene, conjugated dienes, acrolein, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acid anhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles and (alkyl)acrylamides, vinyl halides or vinylidene halides or mixtures thereof.

18. A process according to claim 17 wherein the ethylenically unsaturated monomers are styrene, α -methyl styrene, p-methyl styrene or a compound of formula $\text{CH}_2=\text{C}(\text{R}_a)-(\text{C}=\text{Z})-\text{R}_b$, wherein R_a is hydrogen or $\text{C}_1\text{-C}_4$ alkyl, R_b is NH_2 , $\text{O}^-(\text{Me}^+)$, glycidyl, unsubstituted $\text{C}_1\text{-C}_{18}$ alkoxy, $\text{C}_2\text{-C}_{100}$ alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted $\text{C}_1\text{-C}_{18}$ alkoxy, unsubstituted $\text{C}_1\text{-C}_{18}$ alkylamino, di($\text{C}_1\text{-C}_{18}$ alkyl)amino, hydroxy-substituted $\text{C}_1\text{-C}_{18}$ alkylamino or hydroxy-substituted di($\text{C}_1\text{-C}_{18}$ alkyl)amino, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$ or $-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}^+\text{H}(\text{CH}_3)_2 \text{An}^-$;

An^- is a anion of a monovalent organic or inorganic acid;

Me is a monovalent metal atom or the ammonium ion.

Z is oxygen or sulfur.

19. A process according to claim 11 wherein the ethylenically unsaturated monomer is selected from the group consisting of $\text{C}_1\text{-C}_{18}$ alkyl methacrylate, $\text{C}_1\text{-C}_{18}$ alkyl acrylate, 2-ethylhexyl (meth)acrylate, isobornyl (meth)acrylate, lauryl (meth)acrylate, allyl (meth)acrylate, stearyl (meth)acrylate, acrylic acid, itaconic acid, methacrylic acid, butadiene, vinyl acetate, vinyl versate, styrene, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, vinyl aromatic monomers, divinylbenzene, divinylpyridine, divinyltoluene, diallyl phthalate, ethylene glycol di(meth)acrylate, butylene glycol di(meth)acrylate, divinylxylene, divinylethylbenzene, divinylsulfone, divinylketone, divinylsulfide, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl carbonate, diallyl malonate, diallyl oxalate, diallyl adipate, diallyl sebacate, divinyl sebacate, diallyl tartrate, diallyl silicate, triallyl tricarallylate, triallyl

aconitate, triallyl citrate, triallyl phosphate, N,N-methylene dimethacrylamide, N,N-methylene dimethacrylamide, N,N-ethylenediacrylamide, trivinylbenzene, and the polyvinyl ethers of glycol, glycerol, pentaerythritol, resorcinol, monothio and dithio derivatives of glycols, and combinations thereof.

20. A process according to claim 11 wherein an acid containing unsaturated monomer is added, which is selected from the group consisting of methacrylic anhydride, maleic anhydride, itaconic anhydride, acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acryloxypropionic acid, (meth)acryloxypropionic acid, styrene sulfonic acid, ethylmethacrylate-2-sulphonic acid, 2-acrylamido-2-methylpropane, sulphonic acid; phosphoethylmethacrylate; the corresponding salts of the acid containing monomer, and combinations thereof.

21. A process according to claim 11 wherein a further cationic compound selected from the group of cationic surfactants is added in step A).

22. A process according to claim 11 wherein step B) is repeated with a second ethylenically unsaturated monomer which is different from the first one, leading to a block copolymer.

23. A process according to claim 11 wherein the natural or synthetic clay is selected from the group consisting of smectite, phyllosilicate, montmorillonite, saponite, beidellite, montronite, hectorite, stevensite, vermiculite, kaolinite, hallosite, synthetic phyllosilicates, and combinations thereof.

24. A process according to claim 11 wherein the natural or synthetic clay is montmorillonite.

25. A monomer/polymer clay nanocomposite dispersion obtainable by a process according to claim 11.

26. A composition comprising an aqueous dispersion of a natural or synthetic clay which is partially intercalated and/or exfoliated and a compound according to claim 1.

27. A composition according to claim 26, which contains additionally an ethylenically unsaturated monomer and/or an organic solvent.

28. Use of a compound of formula I or II for the polymerization of ethylenically unsaturated monomers.

29. Use of a monomer/polymer clay nanocomposite dispersion obtainable according to claim 11 as additive in paints, coatings, inks, adhesives, reactive diluents or in thermoplastic materials.

Abstract

The instant invention relates to cationic alkoxyamines, which are useful as polymerization initiators/regulators in a controlled stable free radical polymerization process to produce intercalated and/or exfoliated nanoparticles from natural or synthetic clays. The invention also relates to improved nanocomposites produced by this process and to the use of these nanocomposite compositions as, for example, coatings, sealants, caulks, adhesives and as plastic additives.